MINERAL AND NUTRIENT CYCLES AND THEIR EFFECT ON THE PROTON BALANCE OF A SOFTWATER, ACIDIC LAKE

By

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By

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Mineral and nutrient cycles in a softwater, acidic lake were studied using laboratory experiments, littoral mesocosms, and whole-lake mass balances. The primary study site was McCloud Lake, a small (5 ha), acidic (pH 4.5), seepage lake in the Trail Ridge Region of northcentral Florida.

Titrations of sediment slurries from McCloud Lake and other softwater lakes showed that profundal sediments have an acid neutralizing capacity (ANC) up to 10 meq/100 g dry weight. Cation exchange of calcium and magnesium accounted for over 50% of the ANC in the sediments examined, while solubilization of aluminum accounted for up to 20% of the ANC. Exchanges of sodium and potassium were unimportant, as was sulfate adsorption. An experiment to simulate subsurface seepage to McCloud Lake showed that littoral sediments could neutralize synthetic groundwater (pH 3.4 to 6.8) by sulfate reduction and cation exchange.

Chemical analysis of *in situ* seepage and sediment pore waters confirmed these results.

Water budget calculations showed that McCloud Lake received 90% of its water from precipitation and 10% from subsurface flow. Sulfate entering the lake was lost by an internal sink (sulfate reduction) that accounted for 37 to 73% of the total input. Assimilation and denitrification consumed over 95% of the nitrate entering the lake. Internal sinks for nitrate and sulfate nearly balanced the proton input to the lake. Although the mass balance was not sensitive enough to show the internal source of calcium and magnesium expected from lab experiments, an analysis of historical trends showed that calcium levels have nearly doubled while magnesium levels have increased by 34% during the past 14 years in which the proton concentration has doubled.

Littoral mesocosm and laboratory microcosm experiments showed that nitrification can occur at the sediment-water interface when the pH of the overlying water is as low as 3.5. Sediment respiration did not appear to be affected by pH in the littoral mesocosms. An analysis of historical trends in McCloud Lake nutrient levels revealed no significant changes in major nutrient species during the past 14 years. These results cast doubt on the hypothesis that nutrient regeneration and decomposition are inhibited in acidified lakes.

CHAPTER 1
INTRODUCTION

Background

Numerous studies have shown that precipitation acidity has increased in large areas of Scandinavia and North America (Devland et al. 1976, Cogbill and Likens 1974, Brazonik et al. 1983b). It is widely believed that increased precipitation acidity has resulted in the acidification of thousands of poorly buffered lakes and streams (Grahn et al. 1974, Gjessing et al. 1976, Norton et al. 1980, Schofield 1976, Impact Assessment Group 1983).

Acidification has major and often serious effects on lake and stream ecosystems. In addition to the direct effect of H^+ on osmoregulation (Leivestad et al. 1976), decreased pH affects biota through several indirect mechanisms. Decreased pH enhances the solubility of toxic metals, and increased concentrations of aluminum, cadmium, zinc, and lead have been observed in lakes and streams that have become acidified (Almer et al. 1978, Norton et al. 1980). Humic acids precipitate at low pH, accounting in part for the increase in clarity observed in acidified lakes, and the precipitation of aluminum phosphate complexes may decrease lake phosphorus levels (Almer et al. 1978).

Acidification produces distinct changes in biological communities. The most notable effect has been the decline of fish populations in many rivers and lakes in the Scandinavian countries and in

the Adirondack Mountains of New York (Leivestad et al. 1976, Almer et al. 1978, Schofield 1976). Major changes occur in the structure of phytoplankton and zooplankton communities, and declining pH clearly results in decreased species diversity of plankton communities (Hutchinson et al. 1978, Leivestad et al. 1976, Almer et al. 1978), although it is not clear whether primary productivity decreases (see Hendrey et al. 1976). Grahn et al. (1974) postulated that acidification retards decomposition and nutrient regeneration and initiates a "self-oligotrophication' process, although subsequent studies have produced conflicting results (Schindler et al. 1980, Dillon et al. 1979, Hultberg and Andersson 1982).

Objectives

One of the major problems in acid precipitation research is to elucidate the relationship between precipitation acidity and lake pH. To develop models for this purpose requires an understanding of the processes that produce and consume H^+ ions in lakes and their watersheds. Current lake acidification models are based on watershed weathering reactions (Hendriksen 1980, Wright 1982) and ignore in-lake neutralization processes. Thus, the objectives of the first phase of this study (Chapter 3) were to identify H^+-neutralizing mechanisms that occur in the sediments of softwater lakes and to evaluate the potential of these reactions in neutralizing the overlying water. Chapter 4 addresses the question of in-lake neutralization using a mass balance of major ions for McCloud Lake, Florida, to quantify source and sink terms.

The second phase of this research (Chapter 5) is a study of decomposition and nitrogen cycling in McCloud Lake. The hypothesis

that decomposition and nutrient regeneration are inhibited in acidified lakes has not been thoroughly evaluated, and several recent studies indicate that nutrient levels do not change substantially upon acidification or neutralization of whole lakes (Dillon et al. 1979, Schindler et al. 1980, Hultberg and Andersson 1982). Chapter 5 includes in situ mesocosm and laboratory microcosm studies to evaluate nutrient regeneration, a nitrogen mass balance for McCloud Lake, and an evaluation of historical trends in nutrient levels for this lake.

Site Description

McCloud Lake is a small (5 ha) softwater lake in the Trail Ridge Region of north-central Florida, approximately 40 kilometers east of Gainesville. The region is characterized by karst topography and includes numerous sand hills interspersed by small lake basins that resulted from solution of the underlying limestone.

The 95 ha watershed is uninhabited and is located on the Katherine Ordway Ecological Preserve maintained by the University of Florida. Surficial soils in the watershed are nonspodic marine deposits of fine sand, gravel, and sandy clays of the Citronelle Formation. These surficial deposits are underlain by 24-30 m of phosphatic sands, sandy clays, and clays of the Hawthorne Formation. These clays act as a confining layer (aquiclude) that separates the deep Floridan aquifer from the unconfined, perched water table of the Citronelle Formation (Brezonik et al. 1983a).

The lake is a simple doline (Figure 1-1) with no defined inlets or outlets. Most of the water to the lake comes from direct precipitation, the remainder enters as subsurface seepage. Water levels

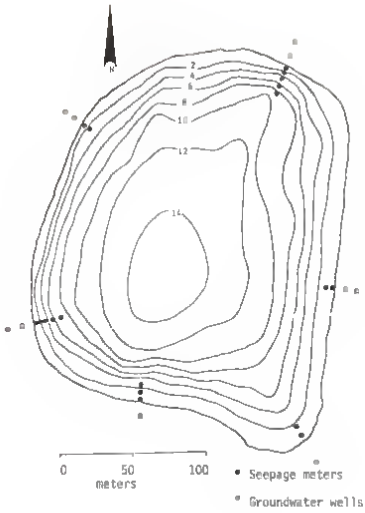


Figure 1-1 McCleum Lake bathymetric map

Table 1-1 Summary of morphometric information for McCloud Lake

Elevation	36.5-38.0 above NVGD[a]
Surface area (at 35.6 m)	4.81 ha
Volume (at 35.6 m)	11.9 x 10^4 m^3
Mean depth	2.5 m
Maximum depth	4.6 m
Watershed area	95 ha

[a]National Vertical Geodetic Datum (approximately mean sea level)

fluctuate in response to changes in relative rates of precipitation and evaporation. During 1980-81, the water level was very low due to a prolonged drought, and the maximum depth was 4-5 m. During 1966-67, the maximum depth was 8.4 m and the lake had a surface area of 9 ha (Brezonik et al. 1969), nearly double the 1980-81 area of 5 ha.

McCloud Lake has very low conductivity (< 50 uS/cm at 25° C) and no alkalinity. The lake has become increasingly acidic during the past 14 years (see Chapter 4), and now has a mean pH of 4.6. The algal standing crop is small (mean chlorophyll *a* was 6 ug/L in 1981), and the phytoplankton community is dominated by six genera: Oocystis, Olnobryon, Mougeotia, Chlamydomonas, Glenodinium, and Euglena (Crisman et al. 1983). A narrow band of emergent macrophytes surrounds the lake, and the sparse submergent macrophyte community is composed primarily of two species: Eleocharis sp. and Websteria confervoides (Crisman et al. 1983).

CHAPTER 2
METHODS

A major problem in evaluating historical data relative to the effects of acid precipitation is the lack of detail provided by earlier investigators on the analytical methods they used. The purpose of this chapter is to provide details of sample collection, preservation, and laboratory analyses used in this study. Experimental procedures are described in the appropriate chapters.

Sample Collection

Throughout this study, samples were collected in linear polyethylene (LPE) bottles that were washed with soap and water, then thoroughly rinsed with distilled water. Samples collected for analyses of pH, sulfate, chloride, and conductivity were stored in bottles that were new at the beginning of the study and were never acid-washed. At the University of Florida, these were rinsed with distilled, deionized water (DDW) following the soap-and-water wash. During later experiments (at the University of Minnesota), bottles for these analyses were purchased new and simply rinsed between use and filled with DDW during storage. Samples for nutrient analyses were stored in LPE bottles that had been soaked overnight in 1 l sulfuric acid (at the University of Florida) or 10 % HCl (at the University of Minnesota), then rinsed with DDW. Nutrient samples were preserved by adding 40 mg/L $HgCl_2$ to the sample bottles (USEPA 1974) or by freezing. Samples for metals analyses were stored in LPE bottles that had been soaked in 10 % HNO_3 and rinsed with DDW, these were acidified

with HNO_3 to reach a pH < 2. Glassware used in sample analyses were washed the same way as collection bottles.

Samples were collected from McCloud Lake using an acrylic Kemmerer sampler and were filtered using in-line Gelman Type A-E glass fiber filters that had been rinsed with 250 mL lake water. In-line glass fibers were also used to collect samples for ^{15}N analysis from the microcosm experiments; filters in this experiment were rinsed with 100 mL HCl + 250 mL DDW. Samples in the sediment titration studies and in the pore water study were filtered using glass fiber filters mounted in a syringe-type holder, the entire apparatus was rinsed with 3 fillings of DDW between samples.

Analytical Methods

Cations

Calcium, magnesium, potassium, and sodium were determined by flame atomic absorption (AA)(Varian Model 175 or Perkin Elmer Model 5000) following methods recommended by the manufacturers. Lanthanum oxide was added to prevent ionization interferences in calcium and magnesium analyses (APHA 1981). Aluminum was analyzed by flameless AA on the Perkin Elmer instrument using settings recommended by the manufacturer.

Nutrients

Nitrogen species (ammonium, nitrite, and nitrate) were generally determined by AutoAnalyzer techniques (Table 2-1). Kjeldahl nitrogen was determined by a scaled-down micro-Kjeldahl technique (APHA 1981) in which 50 mL samples were digested in a block digester. Ammonium in

the digestate was determined by AutoAnalyzer. Nitrate in the pore water study was determined by ion chromatography (described below).

Major Anions

Sulfate and chloride were determined by AutoAnalyzer methods (Table 2-1) for 1) McCloud Lake water, 2) precipitation and seepage meter samples, and 3) samples from the sediment-water microcosms. Ion chromatography (Dionex Model 10) was used to determine sulfate and chloride concentrations in the seepage column experiments and in the pore water study. The ion chromatograph was operated at a flow rate of 40% of maximum (~1.0 mL/min) with a 10 cm pre-column, a 250 cm separator column, and a 250 cm suppressor column (Dow Chemical Corporation).

pH

Analyses of pH were conducted using an Orion Model 911 pH meter with a Corning Model 9i0200 pH electrode at the University of Minnesota) and an Orion Model 901 pH meter with the same probe at the University of Florida. All pH analyses were conducted within eight hours of sample collection. Fischer Certified pH Standards were used to calibrate the pH meter at 4.00 and 7.00 prior to each use. Measurements were made under quiescent conditions, as recommended by Galloway et al. (1979).

Isotope Ratios

Samples for isotope ratio analyses ($^{15}N/^{14}N$) of ammonium from the microcosm experiment (Chapter 6) were prepared by alkaline distillation (APHA 1981) of 400 mL aliquots into 0.01 N H_2SO_4. The first 50 mL of distillate was evaporated to < 2 mL by gentle boiling on a hot plate, cooled, and poured into an AutoAnalyzer tube. To assure

Table 2-1 AutoAnalyzer methods

Parameter	Method and reference[a]	Detection limit, mg/L	Modifications
Sulfate	Methylthymol blue IM 226-72W	0.2	For precipitation samples, $BaCl_2$ and MTB reduced to improve sensitivity
Chloride	Ferricyanide	0.2	Sample cups rinsed with DDW
Nitrate and nitrite	Cd reduction/ diazotization, IM 158-71W/B	0.001	Cadmium wire used instead of granules at U of F
Ammonia	Phenate IM 154-71W/B	0.003	EDTA substituted for citrate-tartrate reagent (APHA 1981) Fresh DDW used for standards In later experiments, standard treated as standard addition to compute NH_3 in DDW
TKN	Kjeldahl digestion APHA 1981	-	Digestion modified by using 50 mL aliquots and block digester NH_3 determined by automated phenate method

[a] IM = Technicon, Inc. Industrial Methods Series

adequate N_2 production for isotope ratio analysis, 1.00 mg N as NH_4Cl was added to each sample prior to distillation. Isotope ratio analyses were conducted by Bill Portier at the University of Florida Soil Science Department using a Micromass 602D double beam mass spectrometer.

Quality Assurance

The correctness of chemical analyses was checked periodically using external quality control standards (EPA "mineral" and "nutrient" standards). A low ionic strength pH standard, prepared using H_2SO_4, was used to check pH calibrations, as recommended by Galloway et al. (1979). Sulfate analysis was used to compute the exact pH of the low ionic strength stock.

Analytical errors were also checked by ion balance calculations. If all significant ions are measured for a water sample, the sum of anions should equal the sum of cations. The difference between these terms can be assumed to represent the analytical errors. Errors in ion balances were calculated from the equation

$$E = \frac{(A^- - M^+)}{(A^- + M^+)} \times 100 \qquad (2\text{-}1)$$

where E = error, as %,
A^- = sum of anions, meq/L, and
M^+ = sum of cations, meq/L.

CHAPTER 3
SEDIMENT BUFFERING IN McCLOUD LAKE

Introduction

The development of models to predict the pH response of lakes to inputs of acid precipitation is a major objective of acid precipitation research. Models currently in use or being developed are either empirical (e.g. Almer et al. 1978) or focus on processes occurring in the watersheds of lakes. Several models treat watershed acidification as a large scale titration in which protons entering the system via precipitation are replaced by cations, principally calcium and magnesium (Henriksen 1980, Wright 1982, Thompson 1982). Other models have been formulated to model short-term variations in streamflow chemistry (Chen et al. 1978, Christopherson and Wright 1981).

The role of pH buffering mechanisms that occur at the sediment-water interface has received little attention in models of lake acidification although Schnoor et al. (1983) included an in-lake neutralization term in their "trickle-down" model. The ability of sediments to neutralize acidity may be particularly important for lakes that have a small ratio of watershed area to lake surface area and receive most of their inflow directly from precipitation. These "Type I" lakes (Schnoor et al. 1983), which are particularly susceptible to acidification, are common in northern Wisconsin and north-central Florida. For example, the 13 soft water lakes in the Trail Ridge Region of north-central Florida surveyed by Brezonik et al. (1983b)

have a mean watershed area lake surface area of 7.0 (range = 1.4 to 20) and a mean pH of 5.2 (Table 3-1). However, the role of precipitation in the water budgets of these lakes is even more important than indicated by the watershed/lake area ratios since much of the precipitation falling on the sandy soils of this region passes directly to the regional water table.

The objective of this chapter is to examine the potential for sediment neutralization of acid in softwater lakes. The addition of acid or base to sediment-water slurries was used to determine the potential magnitude of inorganic neutralization mechanisms under completely mixed conditions. Other experiments were designed to simulate natural sediment-water interactions. Chemical changes that occur during subsurface seepage were evaluated by passing synthetic groundwater through columns of littoral sediment. Acidification experiments involving laboratory sediment water microcosms and littoral mesocosms were used to examine the capacity of sediments to neutralize inputs of acidity to the overlying lake water. Finally, analyses of sediment pore waters were used to evaluate the extent of sediment neutralization processes in situ.

The principal site for this phase of the investigation was McCloud Lake. McCloud Lake is an ideal site for the study of in-lake neutralization mechanisms since the lake receives nearly all of its water directly from precipitation (Chapter 4). Furthermore, the lake has become more acidic during the past 14 years. Water chemistry data collected during 1965-69 (Brezonik and Shannon 1971) and 1978-79 (Brezonik et al. 1983b) show that the pH of McCloud Lake has dropped

Table 3-1. Characteristics of lakes in sediment neutralization experiments.

Lake	Location	Surface area, ha	Mean depth, m	pH	Alkalinity ueq/L	Conductivity uS/cm @ 25° C
Anderson-Cue[a]	Putnam Co., Fla	8	2.0	4.94	10	38
McCleud	Putnam Co., Fla	5	2.0	4.56	0	45
Adaho	Alachua Co., Fla	216	3.6	6.0	54	59
Johnsen	Putnam Co., Fla	140	-	5.24	10	23
Geneva	Clay Co., Fla	650	4.1	6.10	130	65
Clara[b]	Vilas Co., Wis	34	4.6	6.03	49	37
McGrath	Vilas Co., Wis	21	3.0	5.26	-6	18
Sand	Vilas Co., Wis	15	3.2	5.01	-6	27

[a]Data on Florida lakes from Brezonik et al. (1983)

[b]Data on Wisconsin lakes from K. Webster, Wisconsin Dept. Natural Resources

from 5.0 to 4.6. The littoral sediments are generally sandy, interspersed with pockets of peat-like material while the profundal sediments are a soft, highly organic ooze that extend to a depth of approximately 6 meters.

Sediments from four other lakes in the Trail Ridge group and from three lakes in northern Wisconsin were included in the batch neutralization experiments (Table 3-1). Like McCloud Lake, these lakes lack well-defined inlets or outlets and have water with little buffering capacity (alkalinity <200 meq/L) and pH values < 7.0.

Mechanisms for Sediment Buffering

Cation exchange and mineral dissolution are undoubtedly responsible for much of the acid neutralization of watersheds (Henriksen 1980, Thompson 1982). In the well-weathered soils of Florida, kaolinite and gibbsite are the major clay minerals. Both minerals neutralize acidity during congruent dissolution (Stumm and Morgan 1981), kaolinite also has a limited cation exchange capacity (CEC) of less than 10 meq/100 g resulting from isomorphic substitution and from edge charges. In the sensitive watersheds of northern Wisconsin, the dissolution of feldspars and other clay minerals may neutralize acidity. Organic matter, which has a CEC up to 300 meq/100 g, may contribute substantially to the total cation exchange capacity of sandy soils (Yuan et al. 1967) and must be a major component of the total exchange capacity of lake sediments, which often have an organic matter content over 80 %. Humic acids in lakes are known to precipitate upon acidification, a process that consumes protons and may account for the increased clarity observed in acidified lakes (Almer

et el. 1974). Conversely, precipiteted humic ecids may buffer inputs of bese, such as lime, that may be added to neutrelize ecidity.

There is some evidence thet these reections may result in the depletion of cations in surficiel sediments of recently ecidified lakes. Norton et al. (1981) fonnd lower zinc concentretions neer the surfece of sediment cores of 20 lekes in northeestern U.S. end Norway and suggested that the zinc mobilizetion was caused by cation exchange or solnbilizetion of ZnS. Kehl et al. (1982) reported evidence of eccelerated leeching of Ca^{2+}, Mg^{2+}, Mn^{2+}, end Zn^{+2} in surficiel sediments of three ponds in Maine end proposed thet the trend may be the result of recent acidificetion. Neither of these studies (Norton et al. 1981 or Kehl et al. 1982) related the depletion of cations to the hydrogen ion buffering capacity of the sediments. Cetion exchenge wes found to be of minor importance in the neutrelizetion of Lake 223 in the Experimentel Lekes Aree (ELA) of western Ontario during a whole-lake acidificetion project (Cook et el. 1982). However, Lake 223 wes ecidified to only pH 5.1 end it is not known whether cetion exchange may heve played e more significant role in buffering at lower pH levels.

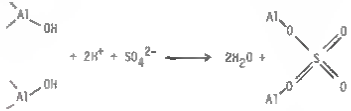
Although the role of sulfete reductron in pH-buffering of sediments is well-known (Nriagu end Hem 1978), this process has received little ettention es e neutrelizetion mechenism in acid-sensitive lakes. The one exceptlon is the study by Cook et el. (1982) which found sulfate reductlon to be a major neutreilzing mechenism in an experimentally ecidified leke. Over a five-year period approximetely half of the H_2SO_4 edded to ELA 223 was neutrelized by sulfate redncrion in the littoral sediments end the anaerobic hypolimnion. This

work clearly suggests the potential for sulfate reduction as a neutralizing mechanism in lakes receiving acid precipitation. Although sulfate reduction in culture is inhibited at pH levels below 5 (Zinder and Brock 1978), this process undoubtedly occurs in neutral microzones in the environment. Several reports indicate that sulfate reduction occurs at significant rates in acidic peat bogs. Hemond (1980) reported that 77% of the SO_4^{2-} entering Thoreau's Bog, Mass., was retained and suggested that dissimilatory reduction may have accounted for approximately half of this loss. Collins et al. (1978) isolated and enumerated sulfate-reducing bacteria, including Desulfovibrio desulfuricans, from a bog that had natural pH levels of 3.0-4.6 but gave no indication of the activity of the organisms in the bog. Rippon et al. (1980) concluded, from SO_4^{2-} and H_2S profiles and $^{35}SO_4^{2-}$ experiments, that sulfate reduction was a significant process in a Danish bog (pH 4.8-6.2). These reports clearly suggest that sulfate reduction may be a significant process in acidic environments, including moderately acidic lakes.

Sulfate adsorption can occur by two mechanisms. Reversible, or non-specific adsorption occurs when SO_4^{2-} acts as a counterion on a positively charged surface (Hsu 1977). In some watersheds, reversible adsorption results in seasonal stabilization of stream sulfate levels. During summer, when precipitation is relatively acidic, soil surfaces become positively charged and SO_4^{2-} is adsorbed. During snowmelt, more neutral water containing less sulfate passes through the soil, surfaces are neutralized and sulfate is desorbed. This process has been in watersheds of the Integrated Lake-Watershed Study (ILWAS) in

the Adirondeck Mountains (Chen et al. 1979) and in the Birkeness watershed in Norway (Christopherson and Wright 1981).

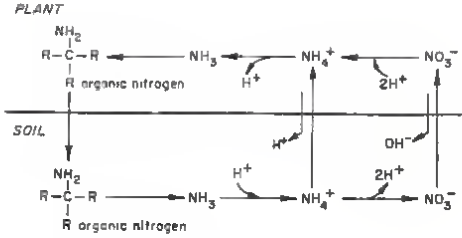
Irreversible sulfate adsorption (also called specific adsorption) involves a substitution of SO_4^{-2} into the inner sphere of a metal hydroxide surface. The mechanism proposed by Rajan (1978) results in the displacement of two hydroxide ions for each sulfate ion adsorbed



(3-1)

Irreversible sulfate adsorption results in a net (permanent) accumulation of sulfate and protons in a watershed. Johnson et al. (1980) reported sulfate accumulation rates up to 9.3 kg/ha-yr for a North Carolina watershed, although many watersheds show a balance between sulfate input and output. Sulfate adsorption has been correlated with iron and aluminum content, clay content and the presence of sesquioxides, and it is inversely correlated with organic content (Johnson et al. 1980). Specific adsorption occurs only under acidic conditions and is not a significant process above pH 6-7.

Reactions of the nitrogen cycle also consume or generate protons in sediment environments (Figure 3-1). Since approximately one-third of the acidity in Florida precipitation is HNO_3 (Brezonik et al. 1983) these reactions are potentially significant in controlling the pH of softwater lakes. In forest and bog ecosystems, most of the nitrate in



Source Impact Assessment Group, 1983

Figure 3-1 Effect of nitrogen cycle on proton balance

precipitation is retained (Kerekes et al. 1982, Hemond 1980, Wright and Johannessen 1980). Retention of nitrate by assimilation into organic matter or by denitrification has the same effect on pH since both reactions consume one H^+ per NO_3^- ion consumed. Although the assimilation of NH_4^+ results in the production of H^+, nitrate deposition exceeds ammonium deposition in Florida and the net effect of terrestial retention of inorganic nitrogen species is the consumption of protons. The effect of nitrogen cycling on the pH of softwater lakes has received little attention. In addition to nitrate and ammonium assimilation, mineralization of organic nitrogen and other reactions of the nitrogen cycle, such as nitrification, could potentially alter lake pH. Although some of these reactions-- notably nitrification and denitrification-- are inhibited at pH levels below 5 in laboratory cultures (NAS 1978), ample evidence indicates that they may occur in acidic environments (see Chapter 5).

Methods

Sediment-Water Batch Experiments

Initial experiments to determine the neutralizing capacity of sediments were conducted by adding 25 g of wet sediment, 100 mL of distilled water, and 1.0 mL of chloroform to 10 Erlenmeyer flasks. Each flask received a single dose of acid (0.1 N H_2SO_4) or base (0.1 N NaOH) and was placed on a shaker table for one week. Upon termination of the experiment, water from each flask was filtered and analyzed for pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, $Si(OH)_4$, and total aluminum. In later experiments, conducted with sediments from Wisconsin lakes, sequential doses of acid or base were added daily, after first determining that the results were similar to those of the single dose method. Several

other modifications included the use of LPE bottles rather than glass Erlenmeyer flasks and the use of 20 g of sediment. After each experiment, the sediment in each flask was dried to 103° C to determine dry weight, and then ashed at 500° C to determine the volatile solids content.

The neutrallzing capacity of the sediments was calculated on a dry weight basis

$$NC_i = 100 \times [V_f N_{a,b} - 10^{pH_i - 10^{pH_o}} (V_f)]/W \quad (3\text{-}2)$$

where V_i = cumulative volume of acid at i^{th} addition, mL,
$N_{a,b}$ = normality of acid or base,
pH_o = original pH (no acid or base),
pH_i = final pH,
V_f = volume of water in flask(including water content of wet sediment), mL,
W = dry weight of sediment, g, and
NC_i = neutralizing capacity of sediment at the i^{th} acid or base addition, meq/100 g.

The exchange of metal cations also was computed on a dry weight basis in order to calculate the contribution of each metal to the total buffering capacity.

The potential for sulfate adsorption by McCloud Lake sediments was evaluated in a separate batch experiment in which a single dose of 0.1 N H_2SO_4 (0.1 to 1.0 mL) was added to each of ten LPE bottles containing 20 g sediment and 50 mL DDW. Since chloroform could potentially alter sulfate adsorption and/or sulfate analysis, the experiment was conducted with and without the addition of 1.0 mL chloroform. The entire experiment was also conducted with a series of bottle blanks that received no sediment. The bottles were placed on a shaker table for a week, upon termination of the experiment water from each bottle was filtered and analyzed for sulfate and pH. Sulfate

adsorption was evaluated by comparing sulfate recovered with sulfate added, after accounting for sulfate levels in controls (no acid added).

Seepage Column Experiment

An upflow column study was conducted to simulate the flow of groundwater through McCloud Lake littoral sediment. The synthetic groundwater used in this experiment (Table 3-2) represented soil water from a depth of 190 cm at a site adjacent to Lake McCloud that had been repeatedly irrigated with simulated pH 3.0 rain (J. Byers, University of Florida, pers. comm.). This soil water was circumneutral (pH 6.6) and contained appreciable alkalinity (estimated by ion balance).

The synthetic groundwater was passed through three 20 cm intact columns of McCloud Lake littoral sediment at a flow rate of ~40 mL/day, which corresponded to the highest seepage rates observed during 1981. Three additional columns received the same groundwater acidified to pH 3.5 with H_2SO_4 (designated "low pH" treatment). A third set of three columns received groundwater acidified to pH 6.2 (through week six) and then acidified to pH 4.0 to observe the effects of rapid acidification. Following a one-month period of pH stabilization, the eluate from each column was collected weekly and analyzed for sulfate, chloride, and nitrate (ion chromatography), alkalinity, major cations, and pH.

Microcosm Experiment

The influence of sediments on the composition of overlying lakewater was simulated in 10 L microcosms containing 1.0 L of

Table 3-2. Synthetic groundwater used in seepage experiments.

Constituent	COMPOSITION OF INFLOW WATER[a]				
	Study site groundwater[b]	Low pH inflow	Intermediate pH inflow		High pH inflow
			Before week 7	After week 7	
pH	6.86	3.47	6.22	4.00	6.56
Ca^{2+}	3.42	3.68	3.44	3.44	3.65
Mg^{2+}	1.09	1.25	1.20	1.31	1.17
K^{+}	1.92	2.21	2.21	2.17	2.22
Na^{+}	4.09	4.31	4.31	4.12	4.26
HCO_3^{-}	13.7	0.00	NA	0.00	13.3
SO_4^{2-}	3.6	35.0	13.3	22.6	3.8
Cl	5.5	5.9	5.5	6.01	5.74
NO_3^{-}	0.33	0.33	0.40	0.33	0.42

[a]Values in mg/L (except pH)

[b]Groundwater from acidified forest plots

McCloud Lake littoral sediment plus 5.0 L of synthetic Lake McCloud water (based on 1981 data). Following a one week period of pH stabilization, duplicate microcosms were acidified to pH 5.0, 4.5, 4.0, and 3.5 using 1.0 N H_2SO_4. An additional set of duplicates was used as controls. Repeated additions of acid were required to maintain the desired pH levels. Acid inputs were based on pH values determined immediately before each addition, the volume of H_2SO_4 added on each date was sufficient to reach the desired pH level in the absence of neutralization. Samples collected after 40 days (prior to the addition of labelled algae and the beginning of the decomposition experiment-see Chapter 5) were filtered and analyzed for alkalinity, sulfate and chloride, major cations, and pH. Components of buffering were inferred by comparing the chemical composition of the microcosms at 40 days with the initial composition.

Littoral Mesocosms

A mesocosm experiment conducted in the littoral region of Lake McCloud to evaluate the effects of pH alterations on biological processes (see Chapter 5) also served as a preliminary experiment on in-situ pH buffering. During March, 1981, three 4.0 m diameter enclosures (designed after Landers 1978) were placed in the lake at a depth of ~1 meter and anchored firmly to the bottom with wooden stakes to enclose an area of 12 m^2. One enclosure was acidified to pH 3.6 with 1.0 L aliquots of 0.72 N H_2SO_4 while a second received 1.0 L aliquots of 0.1 N NaOH to raise its pH to 5.6. A third bag received no acid or base and served as a control. Acid or base was added weekly with the intention of reaching the desired pH level within one month. Continued additions of acid or base were required throughout the 26 week

study to reach or maintain the desired pH levels. During this experiment, samples were analyzed weekly for pH, major cations, sulfate, chloride, and major nutrients.

Pore Water Profiles

Littoral and profundal cores were obtained from McCloud Lake using a Livingston-type corer during February, 1983. Three cores (3.8 cm interior diameter) from each site were dissected into 2.5 cm segments in a glove box that had been purged with O_2-free nitrogen gas. Individual segments were placed into centrifuge tubes, treated with 0.1 mL 2 M zinc acetate and 0.06 mL NaOH to precipitate ZnS (APHA 1981), and centrifuged for 20 minutes at 15,000 rpm. The supernatant was filtered and analyzed for sulfate, chloride, and nitrate by ion chromatography.

Results and Discussion

Sediment-Water Batch Studies

Magnitude of neutralization

Results of the sediment batch studies are shown as buffering capacity curves for the McCloud Lake littoral and profundal sediments (Figure 3-2). Each point in Figure 3-2 represents the neutralizing capacity for a given pH, as calculated from equation 3-2. The profundal sediment had far more neutralizing capacity than the littoral sediment, as seen in the much steeper slope for the profundal sediment. To facilitate comparisons of neutralizing capacities among sediments, neutralizing capacities were computed over defined pH ranges. Thus, the $NC_{4.5-5.0}$ is the neutralizing capacity, expressed as meq/100 g, over the pH range 4.5 to 5.0 and the $NC_{5.0-5.5}$ is the

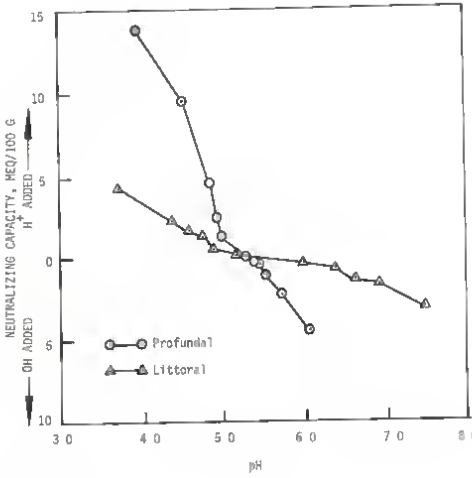


Figure 3-2 Titration curves for McCloud Lake sediments.

neutralizing capacity between pH 5.0 and pH 5.5. As seen in Table 3-3, the profundal sediments typically have $NC_{4.5-5.0}$ values of 8-10 meq/100 g while the littoral sediments, which are considerably more sandy, have much lower buffering capacities ($NC_{4.5-5.0}$ =0.6-1.2 meq/100 g). Although there are not enough data points for sediments having intermediate levels of volatile solids to permit formal regression analysis, it is clear that the volatile solids content, or some factor associated with volatile solids content (such as clay fraction) is strongly related to the buffering capacity of sediments.

Cation exchange

Changes in cation concentrations during titration of the McCloud Lake sediment (Figure 3-3) suggest that ion exchange was the major buffering mechanism. Although mineral dissolution and precipitation could account for these results, minerals containing these cations are probably not present in McCloud Lake. Furthermore, the H^+ neutralization occurred rapidly and was essentially complete within a few hours. This behavior is typical of cation exchange, whereas mineral dissolution, especially of clay minerals, is generally much slower.

When NaOH was added, protons on sediment exchange sites were replaced by cations from solution (primarily Ca^{2+} and Mg^{2+}), and their solution concentrations decreased. When H_2SO_4 was added, base cations on sediments surfaces were replaced by protons, and cation concentrations in solution increased. Calcium and magnesium exchange accounted for over 50% of the total buffering capacity of McCloud Lake sediments throughout most of the pH range (Figure 3-4). Exchange of Na^+ was significant at pH levels over 6 when NaOH was the source of OH^- in the experiment. Thus, some of the Na^+ added displaced protons on the

Table 3-4. Buffering capacity of some Florida and Wisconsin lake sediments

Sediment	Acid neutralizing capacity meq/100 g pH 4.5-5.0	pH 5.0-5.5	Volatile solids % dry wt	Sand % dry wt	Dry weight % wet wt
Littoral					
Anderson-Cue, Fla	1.15	1.0	18.6	30.2	45.8
Adaho, Fla	0.6	0.5	9.0	41.7	47.6
Johnson, Fla	0.6	2.1	11.3	38.0	46.2
Geneva, Fla	-	1.1	12.4	27.5	37.0
McCloud, Fla	1.0	0.5	10.4	-	31.2
Profundal					
McCloud, Fla.	8.3	2.2	73.3	0	8.6
Clara, Wis	8.7	3.3	62.6	0	5.8
McGrath, Wis.	10.3	7.0	37.1	0	3.2
Sand, Wis	9.0	7.0	67.3	0	6.4

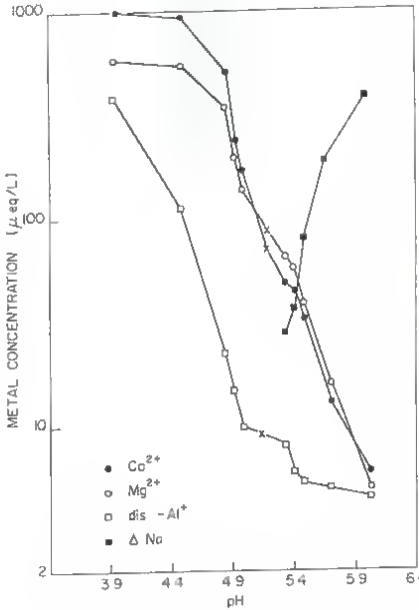


Figure 3 3 Cation concentrations versus pH in batch neutralization experiment with McCloud Lake profundal sediment

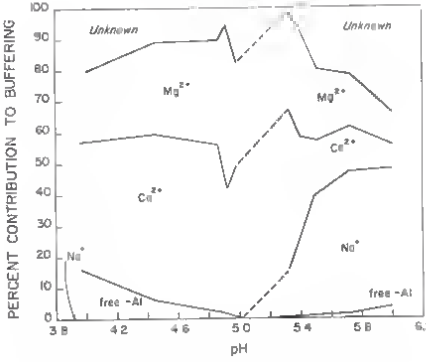


Figure 3-4 Contribution of cations to total neutralizing capacity of McCloud Lake profundal sediment.

sediment surfaces, which contributed to the neutralization of the added OH^-. At pH 6.0, Na^+ exchange accounted for nearly 50% of the total neutralization capacity. Concentrations of dissolved aluminum increased significantly upon acidification, but aluminum solubilization contributed less than 10% to the total neutralizing capacity (even assuming a charge of +3) throughout the pH range 4.0-7.0.

Finally, a portion of the buffering could not be attributed to cation exchange or mineral dissolution. This component increased to 30% of the total neutralizing capacity at pH 6.6 and probably resulted from the dissolution of humic acids. This hypothesis is supported by the observation that the sediment-water solutions became visibly colored at pH levels over 6.0.

Experiments with sediments from other lakes in the Trail Ridge Region and from northern Wisconsin lakes show that exchange of Ca^{2+} and Mg^{2+} is the major mechanism of pH buffering in all of these lakes. Calcium exchange accounted for 41-72% of the total buffering in these lakes, while Mg^{2+} exchange accounted for 20-40% of the buffering in the Florida lakes but only 8-9 % of the total buffering in the three Wisconsin lakes (Table 3-4).

Aluminum solubility

Although dissolution of aluminum accounted for less than 20% the total neutralizing capacity of the Florida lakes (again assuming a charge of +3/mole), aluminum solubility is of interest because aluminum toxicity is a major problem associated with lake acidification. Previous studies (Johnson et al. 1981, Driscoll et al. 1982) have shown that Al^{3+} solubility is controlled by gibbsite, although several

Table 3-4 Components of buffering capacity for selected Florida and Wisconsin lakes titrated to pH 4

Lake	Final pH	% of total neutralizing capacity					
		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	ΣCa+Mg
Johnson	4.46	35.7	39.3	1.2	-	2.5	75.0
Geneva	4.83	63.3	24.7	2.3	-	11.1	88.0
Anderson-Cue	4.07	46.5	22.0	1.2	-	18.4	68.5
Adaho	3.93	46.2	40.0	<.1	-	2.6	86.2
McCloud							
center	3.96	41.2	20.9	0.5	-	15.5	62.1
littoral	3.90	71.8	20.7	25	25	-	92.5
Clara	3.61	44.0	8.9	1.1	1.2	-	52.9
Sand							
center	3.72	49.6	8.3	0.5	1.3	-	57.9
McGrath	3.44	43.3	7.6	0-2	1.0	-	50-5

other aluminum-bearing minerals, including kaolinite, amorphous aluminum hydroxide, and feldspars potentially could control aluminum solubility. Nordstrom (1982) have recently shown that several sulfate-bearing minerals, notably jurbanite ($Al(SO_4)(OH)$) and alunite ($K(SO_4)(Al)_3(OH)_6$), may control aluminum solubility in highly acidic water such as mine drainage.

Total aluminum concentrations in the batch experiments with Florida sediments increased with increasing acidity below pH 5 but were relatively constant (10^{-5} to 10^{-6} M) above pH 5 (Figure 3-5). Also shown in Figure 3-5 are total aluminum concentrations (sum of hydrolysis species) predicted from the solubility of gibbsite (log K = -33.2 from May et al. 1979) and from the solubility of kaolinite (log K=-38.7, Stumm and Morgan 1981). Since silica levels remained nearly constant thoughout the pH range, the mean concentration of 44 uM was used to compute kaolinite solubility. These data clearly show that total aluminum in the sediment titrations was generally above the levels predicted from the dissolution of these two minerals. The most likely reason for the discrepancy between measured total aluminum and predicted solubility is that the measured total aluminum includes organic complexes and fluoride complexes that were not accounted for in these solubility calculations. Driscoll et al. (1982) have shown that organic Al complexes accounted for an average of 44% of the total monomeric aluminum and that Al-F complexes accounted for 28% of the total monomeric aluminum in a group of Adirondack lakes. Fluoride complexes are not likely to be important in McCloud Lake because the lakewater contains very little fluoride (<0.003 meq/L). However, water in the experimental flasks often became visibly colored at pH

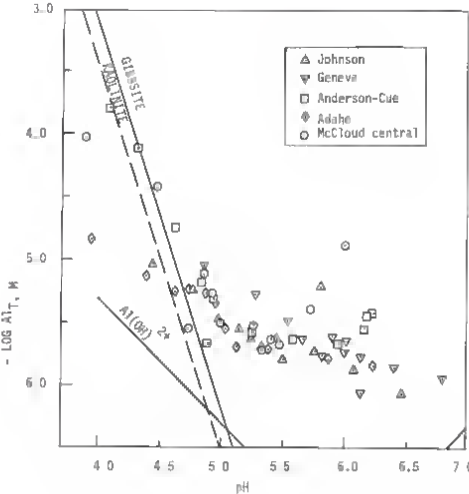


Figure 3-5 Aluminum concentration versus pH in sediment neutralization experiments for five softwater Florida lakes

levels above 5, indicating the solubilization of humic acids. These humic acids undoubtedly formed Al complexes that kept total aluminum levels in solution far above levels predicted on the basis of inorganic complexes. Without further information on the extent of organic complexes, the control of Al solubility cannot be determined precisely.

Solubility calculations for the Trail Ridge lakes, using data from Brezonik et al. (1983b), were conducted with the assumption that total aluminum represented free Al^{3+}. These calculations show that several minerals, including kaolinite, gibbsite, and alunite, may control aluminum solubility. The possibility of alunite precipitation is particularly interesting, since this process would be a sink for sulfate as well as a H^+-neutralization mechanism. However, alunite precipitation would be accompanied by decreased concentrations of K^+ and SO_4^{2-} in the batch studies and these ions were conservative for the McCloud Lake sediments.

Sulfate adsorption

The sulfate adsorption experiment showed that sulfate recovery was at least 100% of sulfate added for both littoral and profundal sediments (Figure 3-6), the addition of chloroform to the bottles had virtually no effect on sulfate recovery in either blanks or treatment bottles. Although it is not clear why sulfate recovery was usually slightly greater than 100%, this experiment shows that sulfate adsorption or other abiotic sulfate-reducing processes, such as the precipitation of alunite or other sulfate-containing mineral (See discussion of aluminum solubility), were unimportant as neutralizing mechanisms within the pH range of this experiment (4.0-5.5).

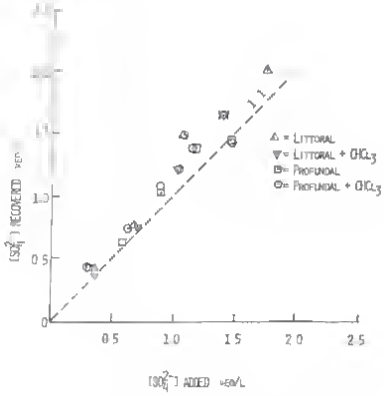


Figure 3-6 Sulfate recovery in batch acidification of McCloud Lake sediments

Seepage Column Experiment

Neutralization of H^+ occurred in the upflow column experiment to the extent that the eluate from all three sets of columns had pH values between 5.0 and 7.0 following the stabilization period (Figure 3-7). Changes in the composition of major ions in the column effluates (Figure 3-8) occurred in all three sets of columns. In the high pH columns (inflow pH = 6.6), concentrations of Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, and NO_3^- decreased, but pH remained nearly constant. During weeks 5-8, the reduction in divalent cations (Ca^{2+} and Mg^{2+}) of 0.20 meq/L was similar in magnitude to the reduction in alkalinity (0.18 meq/L). These results can be accounted for by the following mechanism

$$nHCO_3^- + M^{n+} + nH^+\text{-}X \longrightarrow nH_2CO_3 + M\text{-}X \qquad (3\text{-}3)$$

The inference to be made is that alkalinity and divalent cations leached from the soil by acidic precipitation are removed from seepage water as it passes into the lake through the littoral sediments.

In the low pH columns (inflow pH = 3.5), nearly all (89%) of the influent protons were neutralized by the sediment. Calcium, which was initially retained by the columns (weeks 5-7), later was leached from the columns (Figure 3-8). Although magnesium was leached from the column throughout the study, the extent of leaching increased by week 14. Calcium retention nearly balanced magnesium leaching during weeks 5-8; cation exchange was therefore unimportant in pH-buffering. Of much greater significance was the reduction in sulfate levels. The average loss of sulfate (0.410 meq/L) during weeks 5-8 accounted for 86% of the sum of proton loss plus alkalinity gain. Although sulfate adsorption potentially could account for the observed results, sulfate

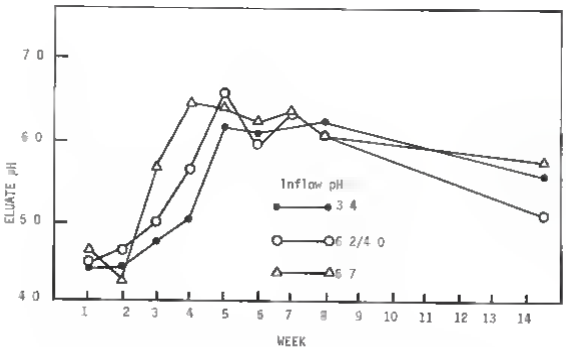


Figure 3-7 pH of eluate passing through 20 cm cores of littoral McCloud Lake sediment.

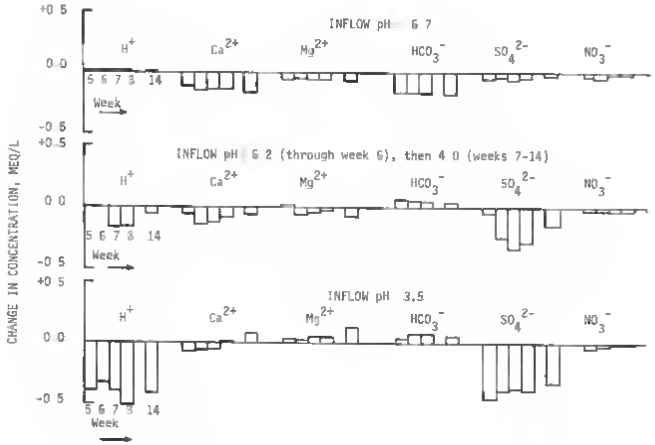


Figure 3-8 Effect of littoral sediments on groundwater eluate in seepage experiment

adsorption was found unimportant in the sulfate adsorption study (see Figure 3-6). Biological sulfate reduction is a more likely mechanism, sulfate entering the columns was either reduced to H_2S and lost to the atmosphere or precipitated in the columns as FeS.

Both sulfate reduction and cation exchange were important H^+-buffering mechanisms in the intermediate pH columns. During weeks 5-6, a loss of sulfate (0.14 meq/L) was exactly balanced by a loss of cations and the pH remained constant. Upon further acidification of the inflow to pH 4.0 during week 6, the loss of sulfate increased to 0.31 meq/L and was accompanied by a comparable increase in the loss of cations. Thus, even with rapid acidification the pH of the eluate remained above 5.0. By week 14 however, sulfate reduction was diminished and the pH of the eluate decreased slightly.

Concentrations of Na^+, K^+, or Cl^- were unchanged in all three sets of the columns. These results support the conclusion from the batch studies that monovalent ions do not contribute to ion exchange buffering in the sediments.

It is interesting to note that NO_3^- concentrations were decreased by 90 % in all columns. This reduction could be the result of either nitrate assimilation or dissimilatory nitrate reduction. Although both reactions consume protons (see Figure 3-1), the level of NO_3^- in the column inflows was so low (< 40 ueq/L) that the effect of nitrate loss mechanisms on eluate pH was minor.

Sediment-Water Microcosms

The McCloud Lake sediment-water microcosms exhibited a substantial capacity to neutralize acid added to the overlying water.

Maintenence of the acidified microcosms at the desired pH levels required continued inputs of H_2SO_4 during the 20-week experiment. As seen in Figure 3-9, predicted pH values, calculated from the cumulative acid additions, were far lower than measured pH levels. By the end of the experiment over 90% of the acid added to each microcosm had disappeared (Figure 3-9). An analysis of major ions during week 7 (prior to the addition of ^{15}N-labelled algae to begin the decomposition experiment described in Chapter 5) was used to determine the components of pH buffering. Alkalinity was not measured due to time constraints but was inferred from the ion balance of other major constituents. As seen in Table 3-5, cation exchange was responsible for over 60% of the total buffering in all of the microcosms. Calcium exchange accounted for 45-60% of the buffering, while magnesium exchange comprised 15-25% of the total buffering. Sodium and potassium concentrations changed little and were unimportant in buffering. Sulfate reduction accounted for 25-40% of the total buffering in the acidified microcosms, although sulfate concentrations actually increased slightly (~15%) in control microcosms. This small increase may have resulted from sulfate oxidation but also may have been the result of experimental error. In the acidified microcosms, cation exchange plus sulfate reduction accounted for 81% to 104% of the observed buffering. As with the groundwater seepage experiment, the importance of sulfate reduction as a buffering mechanism increased with decreasing pH and increasing sulfate concentration.

Littoral Mesocosms

The littoral mesocosms also exhibited a substantial capacity for pH buffering (Figure 3-10). During the first 14 weeks of treatment,

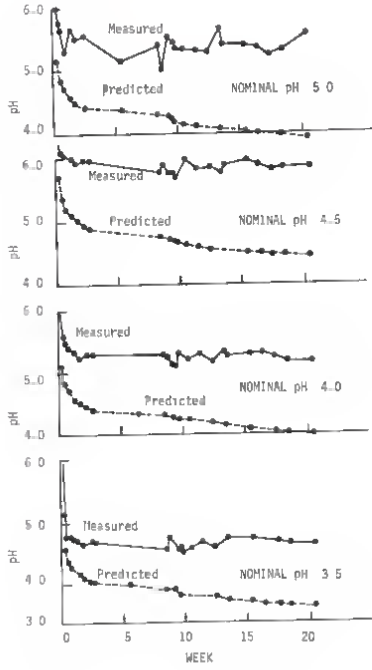


Figure 3-9. pH of acidified sediment-water microcosms

Table 3-5. Buffering components in sediment-water microcosms during first 40 days of acidification

Microcosm	Loss of H^+ + gain of HCO_3^-, meq/L	SO_4^{2-} meq/L	SO_4^{2-} % contribution	Ca^{2+} meq/L	Ca^{2+} % contribution	Mg^{2+} meq/L	Mg^{2+} % contribution	Na^+ meq/L	Na^+ % contribution	K^+ meq/L	K^+ % contribution	Sum of buffering components, % total buffering
3.5	.9192	-0.141	15.3	0.452	49.2	0.156	16.9	-0.013	- 1.4	0.005	0.5	80.5
4.0	.4360	-0.126	29.0	0.248	56.8	0.094	21.6	-0.020	- 4.5	0.003	0.7	103.6
4.5	.2143	-0.048	22.6	0.129	60.1	0.050	23.4	-0.024	-11.2	0.002	1.0	95.9
5.0	.1165	-0.050	43.3	0.052	44.8	0.022	19.1	-0.021	-18.2	0.004	3.3	92.3
5.5	.0959	0.021	-21.6	0.052	54.4	0.024	25.0	-0.016	-16.2	0.006	5.7	47.3

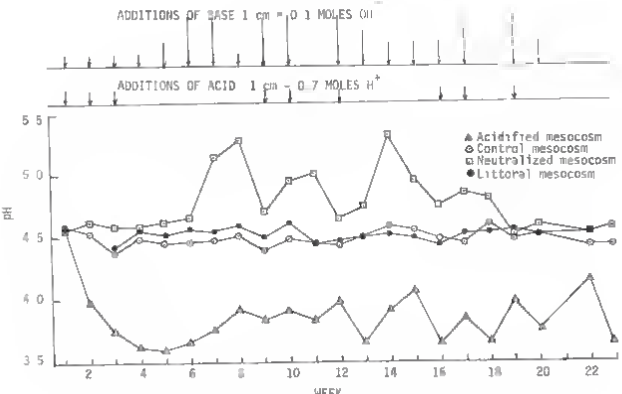


Figure 3-10. Additions of acid and base and pH of McCloud Lake littoral mesocosms.

0.46 meq H^+/L was added to the acidified mesocosm, and 80% was neutralized. While the areal buffering rate of the acidified mesocosm (1.2 meq/m^2-yr) during the first 14 weeks was comparable to the areal buffering rate in the pH 3.5 laboratory microcosms (1.3 meq/m^2-yr), the nature of the buffering was different. Cation exchange, which accounted for 65% of the buffering in the pH 3.5 microcosms, was apparently unimportant in buffering of the mesocosms. Although calcium levels fluctuated considerably during the mesocosm study, there was no sustained increase in calcium or magnesium with acidification (Figure 3-11). The neutralization of added protons was paralleled by a loss of added sulfate, suggesting that sulfate reduction probably was responsible for the neutralization (Figure 3-12).

In the neutralized mesocosm, repeated additions of NaOH failed to cause a sustained increase in pH (Figure 3-10). As in the acidified mesocosm, calcium levels fluctuated considerably, but the expected decrease of calcium and magnesium concentrations did not occur (Figure 3-11). Sodium, however, did disappear, and its rate of disappearance closely paralleled the neutralization of added OH^- (Figure 3-13). The loss of Na^+ is disturbing because Na^+ was conservative in the batch studies below pH 5. The sodium loss may possibly have occurred as the result of water exchange between the mesocosm and the lake, although it is unlikely that the rapid disappearance of OH^- observed during the first month of base additions occurred as the result of water exchange. By week 14, the loss of sodium was equivalent to 71% of the loss of OH^-.

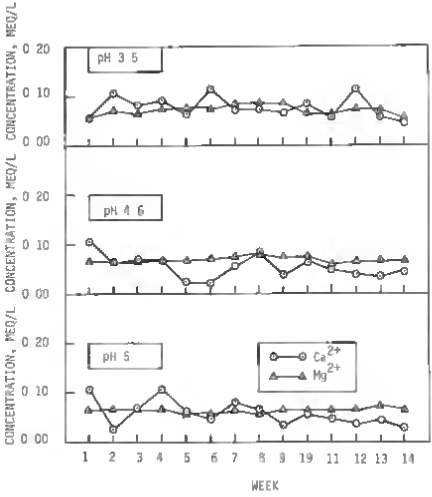


Figure 3-11. Calcium and magnesium concentrations in McCloud Lake littoral mesocosms.

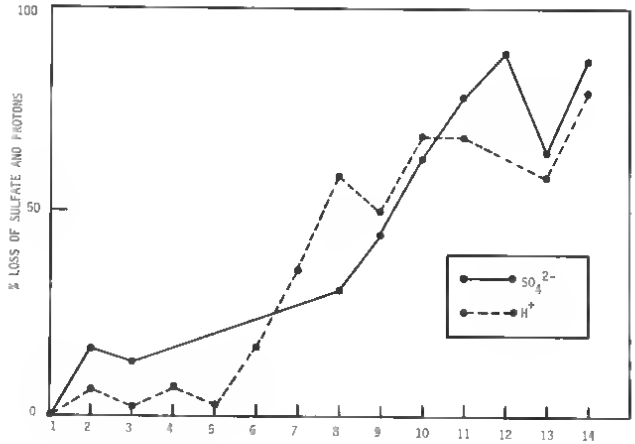


Figure 3-12. Loss of sulfate and protons in the acidified mesocosm

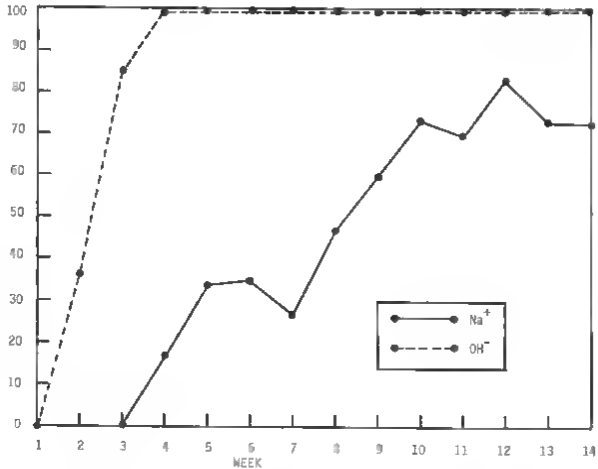


Figure 3-13 Loss of sodium and hydroxide ions in neutralized mesocosm

Precautions taken to prevent mixing of lakewater with the water in the experimental enclosures included anchoring the bottom with stakes and providing a floating collar to minimize wave action, but some exchange undoubtedly occurred. Furthermore, inputs of groundwater and precipitation were not determined and presumably had some effect on the composition of water in the enclosures, even during the relatively short experimental period. In future experiments, it would be useful to use an inert tracer (such as bromide) in control mesocosms in order to ascertain the extent of water exchange between the mesocosms and the open lake.

Pore Water Profiles

The pore water profiles show that sulfate reduction occurs not only in laboratory microcosms but in Lake McCloud itself. As seen in Figure 3-14, sulfate pore water concentrations for the three profundal cores decreased from 150 neq/L in the overlying water to < 15 ueq/L below 10 cm. The flux of sulfate to the sediment in this part of the lake was calculated from Fick's law:

$$F = D_c\{C_i - C_{i+1}\}/z \qquad (3\text{-}4)$$

where D_c = diffusion coefficient, cm^2/sec,
C_i = concentration at depth i, mg/L, and
C_{i+1} = concentration at depth i+1.

According to Lerman (1979), the effective diffusion coefficient, D_c, is approximately equal to $D_\theta\phi^2$, where D_θ is the bulk diffusion coefficent and ϕ is the porosity. Li and Gregory (1974) reported that D_θ for SO_4^{2-} = 8.9 x 10^{-6} cm^2/sec at 18 ^{0} C. If the porosity is estimated from the water content (0.9), Dc is 7.2 x 10^{-6} cm^2/sec. From d = 0 to d = 10 cm, the concentration gradient is 136 ueq/L, so the flux rate of SO_4^{2-} to the profundal sediment is approximately 225

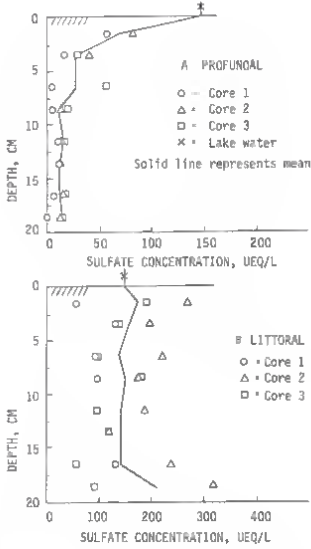


Figure 3 14 Sulfate profiles in pore water of McCloud Lake sediments, February, 1982.

meq/m^2-yr. This rate of sulfate reduction is 54% of the wet-only deposition of 420 meq/m^2-yr for the annual period May, 1981-April, 1982.

Individual pore water profiles in the littoral sediment pore water were very irregular (Figure 3-14), with concentrations ranging from 56 to 320 neq/L. These data suggest that distinct packets of sulfate reduction and oxidation may occur in the sandy, littoral sediments. The irregularity of sulfate reduction was confirmed by the irregular pattern of mottling seen on silver-coated rods inserted in sediment 24 hours prior to collection of the littoral cores. While some reduction and reoxidation may occur in individual core segments, the ratio of SO_4^{2-}/Cl^- in the pore water profile is nearly constant with depth (1.21) and is almost identical to the SO_4^{2-}/Cl^- ratio in the lake water (1.24). Chloride concentrations in the pore water were comparable to lakewater concentations but higher than concentrations in the more dilute in-seepage (see Chapter 4), suggesting that water was moving out of the lake when these cores were taken. The movement of water may have obliterated sulfate profiles that formed during the summer, resulting in the irregular profiles observed. Thus, while this pore water study confirms the occurrence of sulfate reduction in the profundal sediments, there appears to be little evidence of sulfate reduction occurring in the littoral zone.

Conclusions

These experiments demonstrate that reactions at the sediment-water interface are potentially important in neutralizing inputs of H^+ to McClond Lake. The major mechanisms of H^+ neutralization observed

were cation exchange and sulfate reduction. Cation exchange, in which Ca^{2+} and Mg^{2+} were displaced by H^+ on sediment surfaces, provided a neutralizing capacity of up to 10 meq/100 in the profundal sediments. Exchange of Na^+ and K^+ was unimportant, as was sulfate adsorption. Although aluminum was solubilized in the batch experiments, aluminum solubility was relatively unimportant as a neutralizing mechanism. Evidence of sulfate reduction was obtained in the seepage column experiments, in both the mesocosm and microcosm experiments, and in the pore water profiles. This mechanism is interesting because it means that sulfate is not a conservative ion in softwater lakes, as is commonly believed, and because sulfate reduction is a proton-consuming process that may contribute to the neutralization of acid precipitation.

CHAPTER 4
McCLOUD LAKE MASS BALANCE

Introduction

In the previous chapter, results of lab experiments showed that McCloud Lake sediments are capable of neutralizing acid by several mechanisms. Cation exchange, particularly the replacement of divalent cations (Ca^{2+} and Mg^{2+}) by protons resulted in the neutralization of up to 10 meq/100 g dry sediment. Evidence of sulfate reduction was obtained by groundwater seepage and sediment-water microcosm experiments and from *in situ* pore water profiles of sulfate.

The objective of this chapter is to evaluate the magnitude of in-lake neutralization processes in McCloud Lake by constructing mass balances for major ions. Based on the results from the previous chapter, two hypotheses were generated:

1) cation exchange at the sediment-water interface results in the enrichment of the overlying water with base cations, particularly Ca^{2+} and Mg^{2+}, and

2) sulfate reduction in the sediments reduces the quantity of sulfate in the overlying water and neutralizes an equivalent amount of acidity.

A third hypothesis is that assimilation of NO_3^- by phytoplankton and macrophytes, which consumes protons (Brewer and Goldman 1976), is a significant sink for acidity.

Mass balances of major ions entering and leaving McCloud Lake during the period September, 1981-August, 1982 were used to evaluate these hypotheses. Fluxes measured or estimated in the mass balances included wet precipitation, aerosol and gaseous dry deposition, and groundwater seepage to and from the lake. Further evidence of neutralizing mechanisms was obtained by evaluating historical water chemistry data for McCloud Lake collected during 1968-69 (Brezonik and Shannon 1971), 1978-79 (Brezonik et al. 1983b), and 1981-82 (present study).

Background

Mass balance models have been widely used to evaluate the role of watersheds in neutralizing acid precipitation (Johnson et al. 1981, Galloway et al. 1980, Thomson 1982). Cation exchange and mineral dissolution have been recognized as the most important neutralizing mechanisms in watershed soils, and several regional scale sensitivity models are based exclusively on mineral weathering reactions (e.g., Henriksen 1980). Assimilation of nitrate by vegetation in watersheds may also contribute to the neutralizing capacity of forested watersheds. As noted in Chapter 3, the assimilation of nitrate produces hydroxide ions that consume protons. Several studies have shown that most of the nitrate entering forested watersheds is retained with an equivalent number of protons (see Impact Assessment Group 1983). Finally, sulfate adsorption may be an important neutralizing process in some watersheds, particularly those with sesquioxide-rich subsoils (Johnson et al. 1980). In addition to permanent (ligand exchange) sulfate adsorption, reversible adsorption is believed to account for

short-term stabilization of SO_4^{2-} concentrations in watersheds (Chen et al. 1979; Christopherson and Wright 1981).

Few mass balance models have been compiled for sensitive, soft-water lakes and the role of in-lake processes on the H^+ balance of lakes is not well understood. However, several recent reports suggest that anion-consuming processes may be important in regulating lake pH. The potential role of sulfate reduction in neutralizing inputs of acid precipitation to softwater lakes was elucidated by Schindler et al. (1980) and Cook and Schindler (1983). Following the artificial acidification of Lake 223, these authors found that the reduction of sulfate in the anaerobic hypolimnion and littoral sediments accounted for most of the in-lake neutralization in the first two years of acidification (Schindler et al. 1980) and consumed 50% of the total sulfate input during the five years following acidification (Cook and Schindler 1983).

Kilham (1982) reported that acid precipitation may actually increase the alkalinity of non-sensitive lakes. His hypothesis is that the protons in precipitation are neutralized by cation exchange and mineral weathering. Since the consumption of acidic anions (NO_3^- and SO_4^{2-}) also consumes protons (or produces OH^-, i.e. alkalinity), the addition of nitric and sulfuric acids to non-sensitive watersheds can result in an increase in alkalinity production. Kilham (1982) demonstrated that nearly all of the NO_3^- and 66% of the SO_4^{2-} entering the watershed of eutrophic Weber Lake, Michigan, was retained by the lake-watershed system and concluded that nitrate assimilation and sulfate reduction were sufficient to neutralize acid precipitation. Acid precipitation also appeared to have increased the mineralization rate

in the watershed and may have caused a doubling of alkalinity observed over the past 30 years. Kelley et al. (1982) also postulated that hypolimnetic OH^- production resulting from anion-consuming processes may be sufficient to neutralize inputs of acid precipitation to eutrophic lakes.

Finally, in what appears to be one of the only mass balance models reported for an undisturbed, softwater lake, Wright and Johannessen (1980) found that 30% of the H^+ entering Langtern Lake, Norway (6 keq/km^2-yr) was neutralized together with 20% (9 keq/km^2-yr) of the SO_4^{2-}. These authors concluded that sulfate reduction may have accounted for the observed H^+ and SO_4^{2-} depletion.

Methods

Wet Precipitation

Wet-only precipitation was collected using an Aerochem-Metrics Model 101 sampler placed on a raft in the center of McCloud Lake. This sampler is designed so that the wet sample bucket is open only during precipitation events and is tightly sealed with a lid between events to prevent evaporation and contamination by birds, insects, and other debris. Samples were collected monthly and analyzed for pH, major ions, and nutrients.

Dry Deposition

Ambient air concentrations of aerosols (SO_4^{2-}, NH_4^+) and gases (SO_2, NO_2, and HNO_3) were measured during 20 24-hour collection periods during August and September, 1981. Dry deposition rates of these constituents were computed using the equation (Chamberlain and Chadwick 1953)

$$F = V_d \times C_z \qquad (4\text{-}1)$$

where F = areal deposition rate,
V_d = deposition velocity, and
C_z = concentration at a reference height, usually one meter.

Dry deposition rates of other aerosol constituents (Ca^{2+}, Mg^{2+}, K^+, Na^+, and Cl^-) were estimated from two northern Florida data bases. Edgerton (unpublished data) recently conducted a study of dry deposition throughout northern Florida that included one remote site similar to McCloud Lake. The study of Brezonik et al. (1983b) included wet and dry deposition measurements for four inland Florida sites and bulk deposition measurements for 25 sites, including four near McCloud Lake (Gainesville, Jasper, Hastings, and Waldo). Two methods were used to estimate dry deposition of aerosol constituents at McCloud Lake from these data. First, the ratios of wet to total deposition for the four wet/dry collectors were used to estimate dry deposition at McCloud Lake from measured wet deposition. The second method was to subtract McCloud Lake wet deposition from bulk deposition measured at the four local bulk collectors.

Seepage

Seepage flow to and from McCloud Lake was measured using 22 seepage meters (Fellows and Brezonik 1981) placed along six transects perpendicular to the shoreline (Figure 4-1). Flows were measured once a month. When the direction of flow was towards the lake, samples of the inflow groundwater were collected for analyses of major ions and nitrogenous species. Flux rates of water and ions were calculated by dividing the lake into five concentric rings having boundaries that paralleled the shoreline and were equidistant from adjacent seepage

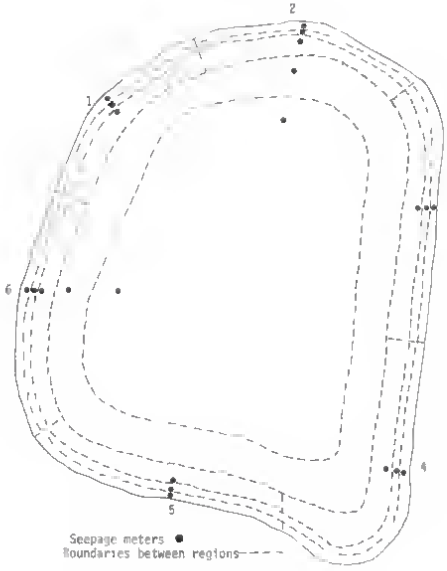


Figure 4-1 McCloud Lake seepage meter transects

meters along each transect. The outer three rings were further divided into 6 subdivisions whose boundaries were equidistant from adjacent transects. Thus, a total of 20 regions were formed, each represented by one, or, for the two inner regions, two seepage meters (Figure 4-1). The flux of constituent i was computed from the equation

$$F_i = \sum_{j=1}^{n} C_{i,j} \times Q_j \qquad (4\text{-}2)$$

where $C_{i,j}$ = concentration of constituent i in seepage region j,
Q_j = flow in region j. (Sign convention: "+" = inflow, "-" = outflow).

Groundwater Wells

Two to four wells (2 " diameter PVC pipes) were placed in the ground along each transect (see Figure 1-1) in order to permit sampling of the local groundwater. During the second half of 1982, samples from these wells were collected for analyses of major ions and nutrients.

Lake Storage

A bathymetric map of McCloud Lake was used to construct stage-volume and stage-area relationships. (See Figure 1-1). Stage measurements were made 2-6 times per month and the mean stage reading was used to compute lake volume and area for the month. Water samples collected monthly at 1-meter intervals near the center of the lake were analyzed for major ions and nutrient species. Since the lake never stratified, storage calculations were based on mean concentrations of samples collected at 3-4 depths.

Evaporation

Pan evaporation measured at Lisbon, Gainesville, and Lake City (Climatological Abstracts 1981 and 1982) was used to compute a distance-weighted mean representative of evaporation at McCloud Lake.

$$E_{dwm} = \sum_{i=1}^{n}(D/d_i \times E_i)/\sum_{i=1}^{n}(D/d_i) \qquad (4\text{-}3)$$

where E_{dwm} = distance-weighted mean of pan evaporation, cm/month,
d_i = distance to station i,
D = total distance, i.e., d_i; and
E_i = pan evaporation at station i, cm/month.

A pan coefficient of 0.70 was used to estimate lake evaporation from the Class A pan evaporation data (Linsley et al, 1975).

Results and Discussion

Water Budget

Components of the McCloud Lake water budget are shown in Figure 4-2 (see Table A-1). To check the accuracy of the water balance, monthly precipitation (P), evaporation (E), and net seepage (G) were used to model the change in storage (ΔS) and the new storage (S) for each month, beginning with the measured storage in August, 1981.

$$\Delta S_i = P_i - E_i + G \qquad (4\text{-}4)$$

$$S_i = S_{i-1} + \Delta S_i \qquad (4\text{-}5)$$

where i = month.

Although the computed S often differed from the measured S for individual months (Figure 4-2), computed S and ΔS agree well with measured values for the entire year. At the end of the year, computed storage was only 2% less than the measured storage, and the computed annual change in storage (+ 17.45 x 10^3 m^3) was 15% less than the measured change in storage of 20.47 x 10^3 m^3. The difference between predicted and measured ΔS was only 3.6% of the total water input (precipitation + in-seepage).

Precipitation accounted for 90 % of the total water input, while in-seepage accounted for the remaining 10%. It should be noted that

the contribution of seepage to the water budget was far less than suggested by the watershed:lake surface area ratio of 20:1. Because of the sandy soils, gentle slopes, and a lack of defined stream channels, precipitation falling on most of the watershed passes directly to a regional water table rather than to a lake or outflow stream.

Although precipitation during the model year was 6% above the 40 year mean, the previous year was very dry and had an annual precipitation of only 57% of the 40 year mean. Thus, seepage during the first seven months of the model year was outward, resulting in recharge of a depleted water table. During the last five months, continued precipitation and a rising water table resulted in seepage flows into the lake (Figure 4-2).

Seepage occurred mainly in the sandy littoral area. As shown in Figure 4-3, seepage rates during both outflow periods (e.g., October, 1981) and inflow periods (e.g., April, 1982) diminished with distance from shoreline. This was particularly evident during the inflow period. During April, 1982, for example, the mean flow rate decreased from 1.1 cm/d at 3 meters from shore to nearly 0 cm/d at 25 m (Figure 4-3). However, since much of the total lake area was in the central low-seepage zone, the central region of the lake was significant in terms of total seepage flow. Thus, 72% of the total outflow but only 4% of the total inflow occurred in the 71% of the lake within the interior of the 17.5 m contour.

The water residence time, based on total inflow (precipitation + seepage), was 1.7 years. Most of the water entering the lake evaporated (63% of the total inflow) and only 16% left the lake via outseepage (the remaining inflow resulted in a change in storage). The

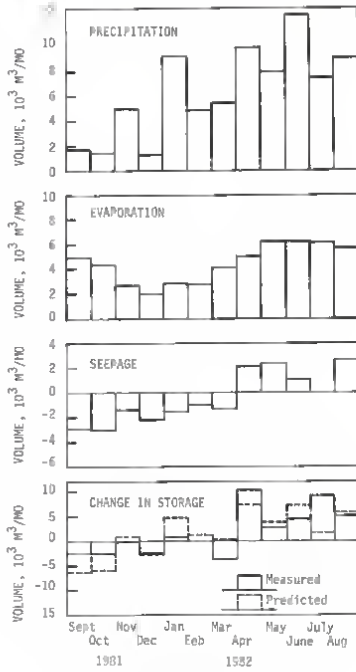


Figure 4-2 Water balance for McCloud Lake, September, 1981, to August, 1982

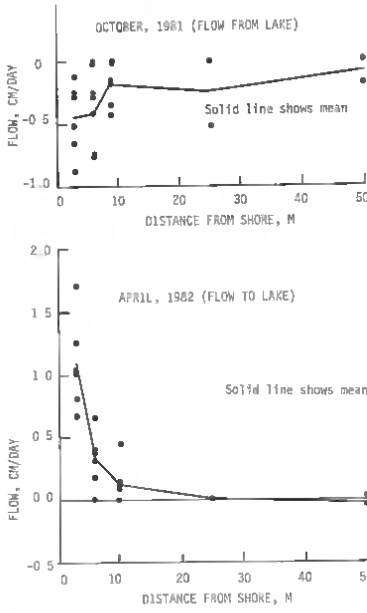


Figure 4-3 Seepage flow versus distance from shore

residence time based on outflow was 9.6 years. Since volatilization of substances other than water entering the lake is minimal or nonexistent, the outflow-based water residence time should be the residence time for conservative ions.

Chemistry of McCloud Lake, Past and Present

Data collected during 1968-1969 (Brezonik et al. 1969), 1978-79 (Brezonik et al. 1983b), and in the current study (Tables A-2 and A-3) allow an evaluation of historical water chemistry trends for McCloud Lake. Before discussing these data, several problems concerning the evaluation of historical water chemistry trends must be considered. The most serious problem with comparing data collected over a span of 14 years is that certain analytical methods have changed significantly. While methods for analyzing cations were similar in all three studies (calcium, magnesium, sodium, and potassium were analyzed by flame atomic adsorption), methods for collecting pH samples and for analyzing sulfate and chloride have changed. In the 1968-69 study, pH samples were collected in glass B.O. bottles "to prevent CO_2 transfer with the atmosphere" (Brezonik et al. 1969, pg. 83). Although Kramer and Tessier (1982) have pointed out that soft glass bottles may contribute 20 - 100 ueq/L alkalinity, the same authors concluded that the use of glass containers would not be be a problem in studies where analyses were conducted immediately following sample collection. In the study of Brezonik et al. (1969), prompt (same day) analysis was done, as inferred by the stated concern for carbon dioxide transfer. Thus, comparisons of the 1968-69 pH data with the data from the two more recent studies (in which pH samples were

collected in distilled water-soaked linear polyethylene (LPE) bottles and analyzed within eight hours) probably are valid.

The most significant methodological change involves sulfate analyses. Sulfate was analyzed by the turbidimetric method in the 1966-69 study (APHA 1971) which, in addition to being an awkward technique, has a detection limit of only 1 mg/L. The reliability of the reported mean sulfate concentration of 2.2 mg/L is therefore questionable. Sulfate analyses in 1978-79 and in the current study were done by the automated methylthymol blue technique, modified to give a detection limit of 0.1 mg/L. Methods of chloride analysis also changed during the 14 year observation period. Chloride in the 1966-69 study was determined by mercuric nitrate titration, using the 'low level' modification (APHA 1971), while in the recent studies chloride was determined by the automated ferricyanide procedure (APHA 1981), also modified to give a sensitivity of 0.1 mg/L. Both techniques, however, are generally free of interferences and considered reliable. Although concentrations of chloride in McCloud Lake are so low that only 1 mL of titrant would be required to reach the endpoint with the mercuric nitrate titration, small bore burets were used to assure that small volumes could be delivered accurately.

The excess of measured anions in the 1966-69 study (10% of the sum of ions) indicates that analytical errors were a problem (Table 4-1). Ion balances were more exact in the 1978-79 study (mean error = 5%) and in the current study (mean error = 3.5 %).

A second problem in evaluating historical trends in acidification is that McCloud Lake undergoes substantial changes in volume as a result of long-term variations in precipitation. Between September,

1981, and August, 1982, for example, the volume increased by 20% because of increased precipitation following several drought years. These volume fluctuations cause changes in the concentrations of dissolved substances by dilution or evaporative concentration that may obfuscate long-term changes in water quality. One way to eliminate changes caused by dilution/concentration effects is to normalize the concentrations of dissolved ions to the concentration of a conservative ion such as chloride. Both concentrations and ion/chloride ratios are shown in Table 4-1.

As shown in Table 4-1, McCloud Lake has become more acidic during the past 14 years. Hydrogen ion concentrations have nearly doubled from 14 ueq/L (pH 4.9) in 1968-69 to 32 ueq/L (pH 4.5) in 1982, while sulfate concentrations appear to have increased from 104 ueq/L in 1968-69 to 142 ueq/L in 1978-79 and 173 ueq/L in 1981-82 (Table 4-1). Reported values of sulfate in 1968-69 may be erroneously high due to analytical problems associated with the turbidimetric method (discussed above), and sulfate levels may have increased more than these data indicate. The excess of measured anions in the 1968-69 data suggests that reported values of one or more anions were too high or that reported cation values were too low.

Increased acidification has apparently resulted in enhanced leaching of base cations. Calcium concentrations in McCloud Lake have doubled from 30 neq/L in 1968-69 to 66 neq/L in 1981-82, while magnesium levels have increased by 34%, from 47 neq/L in 1968-69 to 63 ueq/L in 1981-81. These data must be interpreted with caution because of the poor ion balance associated with the 1968-69 data. The

Table 4-1. Chemical composition of McCloud Lake, 1968 to present.

	1968-69[a]		1978-79[b]		1981-82	
	Conc µeq/L	Ci/Cl[c]	Conc µeq/L	Ci/Cl[c]	Conc µeq/L	Ci/Cl
H^+	14	0.08	19	0.13	32	0.19
Ca^{2+}	30	0.18	47	0.32	66	0.39
Mg^{2+}	47	0.28	51	0.35	63	0.37
K^+	6	0.04	15	0.10	6	0.04
Na^+	122	0.73	121	0.83	153	0.90
SO_4^{2-}	104	0.62	142	0.98	173	1.02
Cl^-	167	1.00	145	1.00	170	1.00
ΣM^+	219	-	253	-	320	-
ΣA^-	271	-	287	-	343	-
% Error	10.5	-	6.3	-	3.5	-

[a] Brezonik and Shannon (1971).

[b] Brezonik et al. (1983b)

[c] Ratio of ion i to chloride.

calcium data are particularly suspect, since ratios of Ca^{2+}/Mg^{2+} have changed significantly since 1968-69. Although the Ca^{2+}/Mg^{2+} ratios in 1978-79 and 1981-82 were close to 1.0, the ratio in 1968-69 was only 0.6. No other investigators have reported such a shift in cation ratios associated with acidification, and it is not clear to what extent the observed trend reflects analytical errors. The early calcium data are particularly suspect since calcium analysis is susceptible to interferences and because an increase in the early calcium values would produce Ca^{2+}/Mg^{2+} ratios closer to 1.0.

Chloride concentrations were relatively stable during this period. Although the mean chloride concentration in 1978-79 (145 neq/L) was slightly lower than the 1968-69 mean (167 ueq/L), the current mean chloride concentration (170 ueq/L) is nearly identical with the 1968-69 mean. These data indicate that dilution or concentration resulting from variations in relative rates of precipitation and evaporation cannot account for the observed differences in H^+, SO_4^{2-}, Ca^{2+}, or Mg^{2+}. Sodium and potassium levels have changed little since the first study, this is consistent with the observation that these ions were nearly conservative in the sediment titration experiments (Chapter 3).

Concentrations of major cations and anions in the lake during 1981-82 are shown in Figures 4-4 and 4-5. Constituents which are derived primarily from precipitation, including sodium, chloride, and sulfate, fluctuated considerably during the study as a reflection of variations in lake volume. Sodium concentrations, for example, increased from 125 neq/L during October, 1980, when the lake volume was 157 x 10^3 m^3 to 229 ueq/L by December, 1981, when the volume had decreased to 120 x 10^3 m^3. As the lake volume increased, sodium

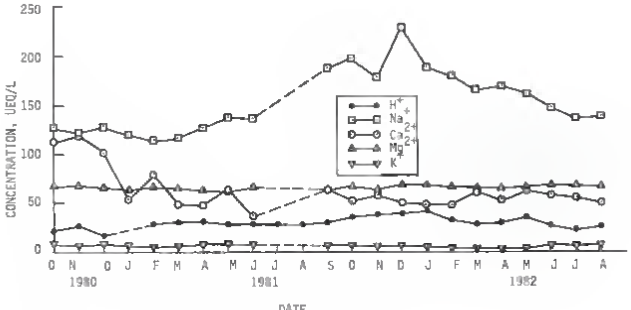


Figure 4-4. Cations in McCloud Lake, 1980-1982.

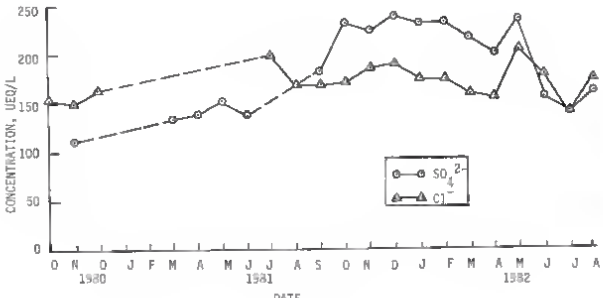


Figure 4-5. Anions in McCloud Lake, 1980-1982

levels declined. By the end of the study, the lake volume had increased to 148 x 10^3 m^3 while the sodium levels declined to 139 neq/L.

Concentrations of other base cations were relatively stable. Although calcium concentrations decreased from 112 neq/L to ~ 60 neq/L during the first three months for some unknown reason, levels were relatively stable throughout the remainder of the study. Magnesium levels were even more stable, concentrations in the two-year study consistently were within ±10% of the mean value. Potassium levels were consistently less than 10 ueq/L and the observed variability at these low levels (4.1 to 8.5 ueq/L) may reflect analytical errors.

Hydrogen ion concentrations show a moderate response to lake volume. Levels increased from 25 ueq/L in October, 1980, to 44 ueq/l in January, 1981, then decreased to 25 ueq/L by August, 1982.

Dry Deposition

Measured concentrations of gases (SO_2, HO_2, and HNO_3) and aerosol constituents (NH_4^+, NO_3^-, and SO_4^{2-}), shown in Table 4-2, were used to compute fluxes of these constituents using equation 4-1. The accuracy of this approach depends on the selection of appropriate deposition velocities (v_d). Deposition velocities depend on the nature of the gas or aerosol, the deposition surface, and meteorological conditions. Published values of v_d for a given substance thus may vary over several orders of magnitude. However, when only one type of surface is considered (in this case, water) the range of deposition velocities decreases. For example, while published values of v_d for SO_2 including all surfaces and conditions span four orders of magnitude (see

Table 4-2 Atmospheric concentrations and fluxes of nitrogen and sulfur species at McCloud Lake site, August-September, 1982

		SO_4^{2-}	NH_4^+	HNO_3	SO_2	NO_2 [a]
Mean concentration, $\mu g/m^3$ (n=20)		2.7	0.4	0.5	3.0	6.0
Deposition velocity (v_d), cm/sec	Low	0.2	0.2	0.5	0.5	0.5
	High	0.6	0.6	1.5	1.5	1.5
Flux, eq/ha-yr	Low	40	14	12	150	210
	High	120	43	36	450	620

[a] Determined at Gainesville

Semmel 1980), deposition velocities for water surfaces under most conditions range from 0.4 to 2.2 cm/sec. Garland (1978) concluded that the mean v_d for SO_2 is approximately 0.8 cm/sec, several researchers have used values of 0.5 to 1.0 cm/sec (Joranger et al. 1980, Edgerton 1981). For this study, the SO_2 flux was estimated using a range of v_d value of 0.5-1.5 cm/sec. Relatively few deposition velocities have been reported for NO_2, NH_3, and HNO_3 (Sederlund 1981). However, since these compounds are highly soluble in water, their deposition to wet surfaces is probably limited by surface resistance (Fowler 1980), and their deposition velocities are probably similar to those for SO_2. Thus, in this study the deposition velocities of these nitrogenous species was estimated as 0.5-1.5 cm/sec.

The value of v_d for sulfate aerosols is less well known. Garland (1978) reported that most of the sulfate aerosol has a diameter of 0.1 to 1.0 um and has a mean deposition velocity of 0.1 cm/sec. However, based on a comparison between measured sulfate deposition in dry buckets (Aerochem-Metrics collector) and ambient air concentrations, Edgerton (unpublished data) has concluded that the mean deposition velocity for sulfate aerosol in Florida is 0.4 cm/sec. Accordingly, values of 0.2-0.6 cm/sec were used to estimate the deposition of sulfate aerosol in this study.

The dry deposition of other aerosol constituents (Ca^{2+}, Mg^{2+}, K^{2+}, Na^{+}, Cl^{-}, and NO_3^{-}) and of NH_4^{+} and SO_4^{2-} was estimated using two northern Florida data bases. Edgerton (unpublished data) has recently collected dry deposition data from four sites in northern Florida using an Aerochem-Metrics wet/dry collector (Table 4-3). These data show considerable variability in deposition rates among sites,

Table 4-3 [illegible]on at five northern Florida sites, 1982

Site	Annual dry deposition, eq/ha-yr				
	Ca^{2+}	Mg^{2+}	K^{+}	Na^{2+}	Cl^{-}
Gainesville	116	70	12	76	60
St Augustine[a]	74	36	12	90	50
Cross City	649	30	12	73	66
Archibald	95	36	12	85	105
Panhandle	33	17	12	37	40

[a]Corrected for sea salt influence.

Source Edgerton, unpublished data.

reflecting local anthropogenic influences. However, the Panhandle site closely resembled the McCloud Lake site in its remoteness from urban areas and its sandy soils and pine-forested surroundings. Deposition rates at this collector were the lowest observed and represent reasonable minimum deposition rates for McCloud Lake. Deposition rates of Ca^{2+}, Mg^{2+}, and K^{+} at this site were used as lower limits of deposition of these constituents McCloud Lake.

The study of Brezonik et al.(1983b) included wet/dry deposition measurements at three inland Florida sites (Gainesville, Belle Glade, and Apopka) as well as bulk precipitation data for 25 sites, including four in the vicinity of McCloud Lake (Gainesville, Jasper, Waldo, and Hastings). Two methods were used to estimate dry deposition at the McCloud site from these data. First, the ratios of wet to total deposition at the three inland wet/ dry collectors (Table 4.4) were used to estimate dry deposition from measured wet deposition at McCloud Lake. This method should produce accurate estimates of dry deposition for substances that have uniform wet/total deposition ratios, such as chloride (wet/total ratios = 0.55-0.59), sodium (wet/ total ratios = 0.55-0.60), potassium (wet/total ratios = 0.55-0.60), nitrate (wet/total ratios = 0.68-0.74), and magnesium (wet/total ratios = 0.40-0.45). For substances such as calcium (wet/total ratios = 0.29- 0.54), sulfate (wet/total ratios = 0.71-0.88), and ammonium (wet/total ratios = 0.73-0.88) this method is less reliable. The second method of estimating dry deposition was to subtract the measured wet deposition at McCloud Lake from the bulk deposition measured

Table 4-4. Relative loadings in wet versus total (wet + dry) precipitation. Values correspond to % deposition from wet-only precipitation

Location	N^{+}	Na^{+}	K^{+}	Ca^{+2}	Mg^{+2}	NH_4^{+}-N	NO_3^{-}-N	Excess SO_4^{-}	Cl^{-}
Gainesville (semi-urban)	100	59	59	31	40	88	68	74	61
Apopka (agricultural)	100	57	55	52	45	73	74	77	61
Belle Glade (agricultural)	100	59	60	40	45	85	72	76	80

at the four regional collectors (Jesper, Gainesville, Waldo, and Hastings) during the 1978-79 study (Table 4-5).

Dry deposition rates estimated from these two data bases are shown in Table 4-6. For each method, some of the measured deposition rates were excluded because they reflect extreme conditions that are not representative of conditions at McCloud Lake. Calcium deposition, in particular, appears to be strongly influenced by local anthropogenic influences, and data from three sites were excluded. Dry deposition of calcium at Cross City (Table 4-3) reflected the proximity of a school playground, whereas bulk deposition of calcium at Gainesville was influenced a parking lot and city streets and bulk deposition of calcium at Jasper reflected phosphate mining activity. Dry deposition of sodium and chloride deposition at St. Augustine and bulk deposition of these ions at Hastings and Jasper reflected a strong sea-salt influence that was not representative of McCloud Lake, and these data were not used. Finally, ammonium deposition at Jasper seemed excessively high (283 eq/ha-yr). Although the reason for the high ammonium deposition is not known, this value was rejected as an outlier.

Dry deposition of alkalinity in the study of Brezonik et al. (1983b) was inferred from the difference between the sum of measured cations and the sum of measured anions (Table 4-5). From Table 4-5 it appears that the inferred alkalinity was approximately 0.6 times the calcium deposition. To estimate alkalinity deposition in this study, this ratio was used in conjunction with estimated calcium deposition.

Dry deposition of NO_2, SO_2 HNO_3, and alkalinity were used to compute an "effective dry deposition" for protons. This computation

Table 4-5. Bulk deposition at four northern Florida sites, 1978-1979.

Site	Bulk deposition, eq/ha-yr							
	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	NH_4^{+}
Gainesville	356	91	33	151	264	508	247	137
Jasper	529	104	80	219	241	670	227	283
Hastings	185	119	58	395	510	450	158	183
Waldo	197	92	61	367	412	617	208	185

Source Brezonik et al (1983b)

assumes that the gases dissolve in water and undergo the following reactions

$$SO_2 + H_2O + 1/2\ O_2 \text{ ----> } SO_4^{2-} + 2H^+ \qquad (4\text{-}6)$$

$$2NO_2 + 1/2\ O_2 + H_2O \text{ ----> } 2NO_3^- + 2H^+ \qquad (4\text{-}7)$$

$$HNO_3 \text{ ----> } H^+ + NO_3^- \qquad (4\text{-}8)$$

The effective dry deposition of H^+ (O_{H^+}) was thus

$$O_{H^+} = O_{SO2} + O_{NO2} + O_{NHO3} - O_{alk} \qquad (4\text{-}9)$$

where O_{SO2}....O_{alk} = deposition rates of subscripted substances, eq/ha-yr.

The last two columns in Table 4-6 show dry deposition rates used in the McCloud Lake model. These values bracket the measured or estimated dry deposition rates for north Florida. Sodium and chloride were further constrained to occur in a ratio of 0.88:1 (the ratio of these ions in seawater--see Stumm and Morgan 1981), although this constraint required very little modification of observed deposition rates (Table 4-6). As shown in Table 4-6, the estimated deposition of Na^+ and Cl^- varied by a factor of three, while estimates of other aerosol constituents varied by factors of three to ten. Estimates of gaseous deposition varied by a factor of three, reflecting the use of v_d values from 0.5-1.5 cm/sec. Deposition rates for NH_4^+ and SO_4^{2-} estimated from aerosol concentrations (Table 4-2) fell within the range of estimates made from bulk and dry collector data. Dry deposition constituents were assigned to three groups: 1) sea-salt components (Na^+ and Cl^-), 2) anthropogenic aerosols (SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, K^+, and alkalinity), and 3) gases (SO_2, HNO_3, and HO_2). To compile the McCloud Lake mass balances, constituents within each group were assigned the upper or lower estimates of dry deposition

Table 4-6. Aerosol deposition at McCloud Lake (all values as eq/ha-yr).

Constituent	Measured wet-only deposition	Dry deposition for north Florida sites[a]	Estimated from wet/total deposition ratio: wet/total ratios	Estimated from wet/total deposition ratio: McCloud dry deposition	Estimated from bulk deposition: Measured bulk deposition at north Florida sites	Estimated from bulk deposition: McCloud dry deposition	Dry deposition values used in McCloud model: Low	Dry deposition values used in McCloud model: High
Ca^{2+}	50	33-115	0.31-0.52	46-111	185-197[b]	135-147	35	200
Mg^{2+}	42	17- 70	0.40-0.45	51- 63	90-120	48- 72	20	70
K^{+}	11	~12	0.55-0.60	7- 9	33- 88	22- 77	10	75
Na^{+}	154	37- 89	0.57-0.59	107-116	191-219[c]	37- 65	35	105
Cl^{-}	180	40-105	0.60-0.61	115-120	241-264[c]	61-84	40	120
SO_4^{2-}	418	80	0.74-0.88	57-147	450-670	32-252	30	250
NO_3^{-}	144	43- 87	0.68-0.44	51- 68	158-247	14-103	10	90
NH_4^{+}	73	-	0.73-0.88	10- 27	127-185[d]	64-112	10	100

[a] Edgerton, unpublished data.

[b] Gainesville and Jaspar included

[c] Hastings, Jasper, and St Augustine excluded

[d] Jasper excluded.

simultaneously. Thus, eight scenarios were constructed representing combinations of high and low sea salts, high and low anthropogenic aerosols, and high and low gases. All combinations of aerosol deposition (i.e., high sea-salt + low anthropogenic aerosols, low sea-salt + low anthropogenic aerosols, high sea-salt + high anthropogenic aerosols, and high sea-salt + low anthropogenic aerosols) had ion balances (equation 2-1) within 5%.

Since deposition of gases contributed to the effective H^+ deposition and the deposition of alkalinity reduced the effective H^+ deposition (equation 4-5), the higher estimate of H^+ deposition was computed using the high estimate of gas deposition and the low estimate of aerosol deposition. Conversely, the lower estimate of H^+ deposition was obtained using the lower estimate of gas deposition and the higher estimate of alkalinity deposition (Table 4-5).

Wet Precipitation

Wet-only precipitation at McCloud Lake, like precipitation throughout northern Florida (Brezonik et al. 1983b), was acidic (volume-weighted mean pH 4.5). The source of H^+ in wet precipitation can be inferred from the anion composition. The occurrence of chloride and sodium in a ratio of 0.86:1 in wet precipitation clearly suggests a sea-salt origin for these ions rather than an HCl source for chloride. The NO_3^- concentration in wet precipitation, 9.8 ueq/L, could account for no more than 34% of the 29 ueq H^+/L. Sulfuric acid was therefore the primary source of protons in wet precipitation the SO_4^{2-} concentration of 29 ueq/L was adequate to account for 100% of the protons in wet precipitation.

Table 4-7 Precipitation chemistry at McCloud Lake, September 1981-August 1982.

Constituent	Wet/only concentration, μeq/L	Wet deposition, eq/ha-yr	Estimated dry deposition, eq/ha-yr		Total eq/ha-yr	% wet	Cl/Cl
			Low	High			
H^+	28.5	420	250	1090	670-1510	28-63	2.2-6.9
Ca^{2+}	3.4	50	35	200	85-250	20-59	0.3-1.1
Mg^{2+}	2.9	40	20	70	60-110	36-67	0.2-0.5
K^+	0.75	10	10	75	20- 85	12-50	0.1-0.4
Na^+	10.5	150	35	105	185-255	59-81	0.86
Cl^-	12.3	180	40	120	220-300	60-82	1.0
Sulfur (total)[a]		420	130	700	600-1120	37-70	2.0-5.1
SO_2 (gas)	-	-	150	450	- -	-	-
SO_4^{2-}	28.5	420	30	250	450-670	37-93	1.5-3.0
NO_3^- (total)[a]		140	230	750	370-890	16-38	1.2-4.0
NO_2 (gas)	-	-	210	620	- -	-	-
HNO_3 (gas)	-	-	10	40	- -	-	-
NO_3	9.8	140	10	90	160-230	61-93	0.6-1.1
NH_4^+	5.0	75	10	100	85-175	76-86	0.3-0.8
Alkalinity	0	0	20	120	20-120	0	0.1-0.5

[a]Includes wet + aerosol + gas species

Wet precipitation accounted for 60-82% of the chloride, 59-81% of the sodium, 62-93% of the nitrate, 75-88% of the ammonium, and 37-93% of the sulfate deposition to McCloud Lake. Gaseous deposition was an additional major source of sulfate and nitrate. Sulfur dioxide (SO_2) deposition, estimated to be 150-460 eq/ha-yr (expression on equivalent basis assumes conversion to SO_4^{2-} at lake surface), was 25-40% of the total sulfur deposition. The adsorption of NO_2 at the lake surface contributed 210-620 eq NO_3^-/ha-yr, or 57-70% of the total NO_x (NO_3 + NO_2 + HNO_3). Interestingly, although SO_4^{2-} was the dominant acidic anion in wet-only precipitation, the dry deposition loading of NO_x was equal or greater than the dry deposition of SO_4^{2-} + SO_2 (Table 4-7).

Dry deposition of H^+ (equation 4-10) was a major source of protons to McCloud Lake. Although the range of estimated values was large (250-1080 eq/ha-yr), these estimates show that deposition of gaseous species (primarily SO_2 and NO_2) may be an important source of protons to McCloud Lake, and may account for 54-71% of the total proton deposition.

Groundwater Chemistry

Table 4-8 shows water quality data for the 12 wells sampled during May-October, 1982 (arithmetic means) and for the 1982 in-seepage (flow-weighted means). These data show that precipitation passing through the soils surrounding McCloud Lake was altered by several mechanisms, even though these soils are extremely sandy and permeable. First, evaporation concentrated the precipitation, resulting in increased concentrations of conservative ions such as chloride and sodium. Based on observed chloride values, well water

Table 4-8. Chemistry of groundwater at McCloud Lake

	Seepage Meters			Well Water		
Constituent	Conc. μeq/L	C_i/Cl	E.F.	Conc μeq/L	C_i/Cl	E.F.
H^+	1.5	0.05	0.007-0.03	1.9	0.02	0.003-0.01
Ca^{2+}	92	2.36	1.6 -7.9	204	2.27	1.4 -7.6
Mg^{2+}	51	1.30	2.6 -6.5	90	1.00	2.0 -5.0
Na^+	34	0.87	1.0	91	1.01	1.0
K^+	20	0.50	1.3 -5.0	37	0.41	1.0 -4.0
SO_4^{2-}	36	0.92	0.2 -0.3	49	0.54	0.1 -0.2
Cl^-	39	1.00	-	90	1.00	-
NH_4^+	3	0.09	0.1 -0.2	-	-	-
NO_3^-	4	0.10	02 - 07	4.5	05	0.01-0.03
HCO_3 [a]	123	3.14	-	280	3.11	-

[a]Inferred from ion balance

was concentrated by e factor of ~4 while in-seepege was concentrated by e factor of ~3 (Table 4-8). The fact that in-seepage wes less concentrated than well water suggests that seepege flows to the lake originated as precipitetion that fell very near the lake shore and passed rapidly through the soil and into the lake. Groundwater further from the lake apparently remains in the soil longer and becomes more concentrated by further evaporetion.

Both seepage end well water had pH values between 5.5 end 6.0. Neutrallzation of precipitation acidity probably occurs as the result cetion exchange thet produces both elkallnity end dissolved Ca^{2+} and Mg^{2+}. This enrichment can be seen by comparing ion/Cl^- ratios in the seepage and well water with the ion/Cl^- retios in the total (wet + dry) precipitetion nsing an enrichment factor (EF)

$$EF = \frac{(C_j/Cl^-)}{(C_j/Cl^-)_p} \qquad (4\text{-}10)$$

where $(C_j/Cl^-)_j$ = ratio of ion j to Cl^- in compartment j;
$(C_j/Cl^-)_p$ = precipitetion ion/Cl^- retio.

An enrichment factor of < 1 indicates e depletion of the ion resulting from chemical precipitation or assimilation, while an enrichment factor > 1 indicates enrichment from mineral dissolution or mineralizetion. An EF of 1.0 indicates thet the ion is conservative.

As seen in Table 4-8, calcium was enriched by a factor of 1.6-3.0 in both the well water and in-seepege, while magnesium was enriched by a factor of 2.6-6.5 in the seepege end 2.0-6.0 in the wells. Alkelinity, calculated by inference from the ion balence, roughly balences Ca^{2+} Mg^{2+} in both seepage and well water. Potassium may also heve been enriched in the seepage and well waters, elthough when the lower estimates of K^+ dry deposition were used to compute the EF,

potassium appeared to be conservative in both compartments (Table 4-8).

Sulfate was depleted in both seepage water (EF = 0.2 - 0.3) and in well water (EF = 0.1-0.2). Sulfate adsorption or biological assimilation was probably responsible for the sulfate depletion in the well water although sulfate reduction could deplete sulfate if the well water became anaerobic. Sulfate reduction undoubtedly caused the sulfate depletion in the seepage water, since this process occurred in the laboratory seepage experiment (Chapter 3).

Both nitrate and ammonium were depleted in the subsurface waters. Much of this depletion undoubtedly occurs as the result of assimilation of these nutrients by terrestial vegetation and soil microorganisms. These results are consistent with reports that inorganic nitrogen is retained in forest soils (Impact Assessment Group 1983). Denitrification in littoral in-seepage also may account for some of the nitrate depletion; laboratory seepage column experiments (Chapter 3) also showed a dramatic reduction of nitrate in the eluate.

Fate of Major Ions in McCloud Lake

Data on wet and dry precipitation, seepage flows, and changes in storage were used to evaluate the fate of ions entering McCloud Lake. Several approaches were used to evaluate in-lake sinks and sources of ions. Annual mass balances were compiled for major ions and nitrogen species using the equation

$$dM/dt = P + G_{in} - G_{out} + S \qquad (4\text{-}11)$$

where dM/dt = change in storage, eq,
P = precipitation (wet + dry) inputs, eq/yr,

G_{in},G_{out} = groundwater inputs and outputs, respectively, m^3/yr, and
S = sink (negative value) or source (positive value), eq/yr.

This approach has the advantage of not requiring steady state conditions. However, evaluation of the sink/ source term is sensitive to errors that result determining small differences between large numbers. This problem is discussed in greater detail with respect to the chloride mass balance below.

Sinks and sources of major ions also were evaluated by comparing the ion/chloride ratios in the inflow (wet + dry precipitation + inseepage) to ion/chlorides ratios in the lake. Since chloride is conservative in aquatic systems, the ion/chloride ratio of a substance entering the lake can change only occur as the result of sinks or sources of that substance within the lake. The magnitude of the sink for substance i (S_i) can be evaluated as

$$S_i = \frac{L_i/L_{Cl} - [C_i]_L/[Cl]_L}{L_i/L_{Cl}} \times 100 \qquad (4\text{-}12)$$

where L_i,$_{Cl}$ = annual input of substance i and chloride, eq/yr,
$[C_i]_L$, $[Cl]_L$ = concentration of substance i and of chloride in lake, meq/L, and
S_i = sink/source term , as per cent of input.

Although this approach assumes that the lake is at steady state, it does not depend on measured changes in storage and is less sensitive to errors in input load. Input loads and mean storage were also used to compute the residence time (T) for various substances entering McCloud Lake, where

$$T = \frac{\text{mean storage, eq}}{\text{annual input, eq/yr}} \qquad (4\text{-}13)$$

The residence time of conservative substances such as chloride and sodium is the same as the water residence time based on outflow.

Shorter residence times indicate that a substance has an internal sink, while longer residence times indicate an internal source.

Chloride

Most of the chloride entering McCloud Lake came from wet + dry precipitation (Table 4-9), groundwater seepage accounted for < 25% of the total chloride input. Although the mass balance equation for the 1981-82 model year indicated a source of 4960-5370 eq/yr, chloride was undoubtedly conservative and the calculated source reflects a problem with the mass balance calculation. Since the mass balance equation (equation 4-11) computes the sink/source term as the difference between inputs, outputs, and the change in storage, it is subject to errors that accrue from estimating small differences between large numbers. The change in storage term is the most likely source of error. During the model year, storage of chloride increased by 4470 eq (20% of the mean storage), compared with an annual precipitation input of only 1120-1520 eq. However the change in storage term is subject to errors in both chloride measurement and estimation of water volume. The error term can be calculated from the equation

$$E_{dM/dt} = E_{C1}*V_1 \pm C_1*E_{V1} \pm E_{C2}*C_2 \pm V_2*E_{C2} \qquad (4\text{-}14)$$
$$\pm E_{C1}*E_{V1} \pm E_{C2}*E_{V2}$$

where $E_{dM/dt}$ = error in change in storage for a given constituent,
$V1, V2$ = initial and final volume,
$C1, C2$ = initial and final concentration,
E_{V1}, E_{V2} = error in initial and final estimates of volume, and
E_{C1}, E_{C2} = error in initial and final estimates of concentration.

If each measured term had an error of only 5% of the true value, and if initial and final storage were approximately equal, the potential error in dM/dt could be as high as 25% of the mean storage. Although

Table 4-9 Fate of ions entering McCloud Lake

Constituent	Precipitation, eq/yr	Seepage		Mean storage eq	ΔS, eq/yr	Sink, source[a] eq/yr	% loss from ion ratios[b]	Residence time (τ) yr
		In eq/yr	Out eq/yr					
Cl^-	1120-1820	340	2360	22,440	+4470	5370+ 4860	-	12 0-15 4
Na^+	1000-1360	300	2620	23,340	-3540	-1360+-1220	11	13.5-17 2
SO_4^{2-}	2990-5580	320	2790	24,360	+ 220	- 230+-2820	39-73	4 1- 7 4
Ca^{2+}	460-1290	810	750	7,050	- 320	- 840+-1560	63-77	3 4- 5 6
Mg^{2+}	570- 320	460	890	8,460	-1950	-1820+-2070	7 56	8.4-11.1
K^+	100- 430	170	80	740	+ 230	+ 30+- 300	78-92	1 2- 2 7
H^+	3300-7560	-480	20	4,100	- 90	-2440+-1815	89-96	0 [illegible] 1.5
NH_4^+	420- 880	30	80	600	- 990	-1350+-1815	89-96	0 [illegible] 1 [illegible]
NO_3^-	1910-4570	30	80	670	- 320	-2140+-4810	97 99	[illegible] 1

[a] '+' - source, '-' - sink Estimated from annual mass balance (equation 4-11)

[b] See equation 4-12

this example represents a worse-case scenario (all errors in the same direction), it illustrates the type of problem encountered in using a mass balance model for a substance that has a large storage relative to inputs during the modeling period. For chloride, with a residence time of 12.0-15.4 years in McCloud Lake, a much longer modeling period would be needed to accurately estimate the sink/source term.

Sodium

Precipitation was also the major source of sodium to McCloud Lake, accounting for 77% of the total input. The mass balance equation indicates a sink of 1360 to 2220 eq/yr, but this is < 10% of the mean storage and is probably insignificant for reasons discussed above. Calculations based on Na^+/Cl^- ratios indicated a small sink (11% of annual inputs), suggesting that sodium is nearly conservative. The residence time for sodium in McCloud Lake, 13.5 to 17.2 years, is very near that of chloride.

Sulfate

Wet + dry precipitation accounted for over 90% of the total inorganic sulfur ($SO_4^{2-} + SO_2$) to McCloud Lake (Table 4-9). Both ion ratios and the annual mass balance indicate that the lake was a sink for sulfate. Although the mass balance yields a sink of 230 to 2820 eq/yr, the magnitude of this sink is small relative to the lake storage of 24,360 eq and therefore subject to the type of errors discussed above. The presence of a sink is confirmed, however, by ion ratio calculations which indicate that 39-73% of the inorganic sulfur entering the lake is lost internally and by the calculated residence time of only 4.1 to 7.4 years.

The most likely mechanism for an internal sulfate sink is biological sulfate reduction at the sediment-water interface. This hypothesis is strongly supported by the sulfate pore water profiles (Figure 3-14), which show a distinct gradient of sulfate in the profundal sediments, and by the seepage column experiments, which showed a loss of sulfate in the groundwater eluate (see Chapter 3). These data alone do not conclusively prove that biological sulfate reduction is responsible for the observed sulfate sink since end products (FeS or H_2S) have not been identified. On the other hand, sulfate adsorption did not occur to an appreciable extent in McCloud Lake sediments (Chapter 3), and it is unlikely that other mechanisms such as biological assimilation or chemical precipitation of sulfate-bearing minerals (Nordstrom 1982) could account for the observed sink. Furthermore, the organic-rich sediment (over 90% volatile solids in the profundal sediments) and warm temperatures (annual mean - 20^{0} C) are conducive to sulfate reduction in McCloud Lake. Although there is some evidence that sulfate reduction may be inhibited below pH 5 (Zinder and Brock 1978), the pH of McCloud Lake sediments is generally above 5, perhaps as a result of the pH-buffering effect of the sulfate reducers. Sulfate reduction has been observed in other acidic environments including peat bogs (Rippon et al. 1980) and experimentally acidified Lake 223 (Kelley et al 1982). The evidence for sulfate reduction in McCloud Lake suggests that sulfate reduction may be an important sink for sulfate in acidic seepage lakes.

Calcium, magnesium, and potassium

Mass balance calculations and comparisons of ion/Cl^- ratios of inputs and lakewater indicate that McCloud Lake is a sink for all three cations. Ion ratio calculations, for example, show that 53-77% of the calcium, 7-45% of the magnesium, and 78-92% of the potassium entering the lake is lost through an internal sink. Potential sinks, such as biogenic accumulation or precipitation of inorganic solids, are unlikely to be important in McCloud Lake. Potassium generally is assumed to be conservative. Potassium concentrations are rarely affected by phytoplankton blooms (Wetzel 1975), K^+ was essentially nonreactive in the neutralization experiments described in Chapter 3, and there are few potassium-containing minerals that would precipitate in a softwater lake. Chemical precipitation of calcium and magnesium is also unlikely in this lake. It therefore appears that inaccuracies in the estimated inputs of these cations are responsible for the apparent sinks. Of the input components, wet deposition is undoubtedly the most accurate. Dry deposition for these elements was estimated only to within a range of approximately one order of magnitude, although the values used undoubtedly bracket the actual dry deposition rates.

The term most likely subject to errors is in-seepage. As shown in Table 4-9, in-seepage was a major source of calcium (39-64% of the total loading), magnesium (44-58% of the total loading), and potassium (29-62% of the total). Furthermore, a large (50%) error in calculated in-seepage would be nearly undetectable in the water balance, since in-seepage only accounted for 10% of the total inflow to the lake. For example, a 50% reduction in in-seepage would change the computed end-of-year water storage by only 3% but would decrease the total calcium

loading by as much as 32% and increase the residence time to 4.4-8.2 years. It is apparent that more intensive sampling of seepage would be required to obtain accurate estimates of fluxes of these cations in McCloud Lake. It should be noted that seepage was a minor source of sulfate, protons, chloride, sodium, nitrate, and ammonium, and relatively large errors in seepage loadings would have minimal effect of budgets of these substances.

Nitrogen species

Wet + dry precipitation accounted for nearly all (over 95%) of the inorganic nitrogen input to McCloud Lake. The total NO_3^- load (including NO_2 and HNO_3 adsorption at the lake surface) was 1940 to 4610 eq/yr, about five times that of NH_4^+ (450-910 eq/yr). Both species of nitrogen were removed from the water column by in-lake mechanisms. The mass balance indicated an annual sink of 1350-1820 eq for NH_4^+ (several times the mean storage of 603 eq) and NH_4^+/Cl^- ratios show that 86-95% of the NH_4^+ entering McCloud Lake was removed. Nitrate had an annual sink of 2140-4610 eq during the model year, compared with a mean storage of 570 eq. Ion ratio calculations indicated that 97-99% of the input nitrate disappeared via an internal sink. The residence times for these substances is approximately one year. Biological assimilation by phytoplankton, bacteria, and macrophytes and the accumulation of organic nitrogen in the sediment are probably the most important mechanisms for removing inorganic nitrogen from the water column of McCloud Lake. Additional loss of NH_4^+ may occur as the result of adsorption to sediment surfaces and additional

loss of nitrate may occur via denitrification. A detailed discussion of the nitrogen cycle in McCloud Lake is presented in Chapter 5.

Proton balance

Nearly all of the protons entering McCloud Lake come from wet precipitation or are the the result of gaseous deposition of SO_2, NO_2, and HNO_3 directly to the lake surface. Seepage inflows contributed 480 eq/yr of alkalinity (which was considered in calculations a negative proton contribution) that neutralized 6-13% of the protons entering the lake via precipitation. The lake was a sink for protons. The mass balance and the ion ratios both indicate that 86-94% of the input protons were lost by an internal sink. Potential mechanisms to remove H^+ in McCloud Lake include sulfate reduction, nitrate assimilation, and cation exchange. Sulfate reduction, which accounted for a loss of 38-73% of the input sulfate, or 1290 to 4390 eq/yr (based on ion ratio calculations), consumed an equivalent amount of protons and was therefore a major sink for protons in McCloud Lake. Nitrogen transformations were also important proton sinks. Assimilation of NH_4^+ by organisms results in the release of protons (1 eq H^+ released/eq NH_4^+ assimilated) to the environment, while assimilation or denitrification of NO_3^- consumes protons (1 eq H^+ consumed/eq NO_3^- consumed). Since nitrate input was approximately five times that of ammonium input, the net result was a consumption of 1880-4550 eq NO_3^- minus 400 to 870 eq NH_4^+, or as much as 1010-4150 eq H^+/yr. Cation exchange of protons entering via precipitation with cations absorbed on sediments may be a significant mechanism--as suggested by results of laboratory experiments in Chapter 3-- but the mass balance

developed in this study was not sensitive enough to evaluate the magnitude of this process.

CHAPTER 5
DECOMPOSITION AND NITROGEN CYCLING IN McCLOUD LAKE

Introduction

Grahn et al. (1974) proposed that acidification of lakes induces a "self-oligotrophication" process in which decomposition and nutrient regeneration are retarded, resulting in decreased productivity in the water column. Although synoptic studies often show a decrease in nutrient levels with decreasing pH (Almer et al. 1974, Crisman et al. 1980), it not clear whether decreased pH causes a decrease in nutrient regeneration or whether the relationship between low nutrient levels and low pH occurs because nutrient-poor lakes also are most susceptible to acidification. Few studies have attempted to quantify the relationship between pH and decomposition rates, and even less work has been directed towards the effects of pH on the mineralization and cycling of nutrients.

The objective of this chapter is to examine the effects of low pH on decomposition and nitrogen mineralization in McCloud Lake. Littoral sediment-water mesocosms (immobags) were used to observe effects of pH alterations on nutrient levels and to conduct studies of sediment metabolism. Laboratory microcosms, with and without sediment, were used to determine effects of pH on nutrient regeneration under more closely controlled conditions. Finally, measurements of all nitrogenous inputs and in-lake nitrogenous species were used to evaluate historical trends, to determine sources and sinks of nitrogen

in the lake, and to evaluate the role of atmospheric nitrogen inputs in lake productivity.

Background

Effects of Low pH on Decomposition

Relatively few studies have been conducted to evaluate the role of pH on the decomposition process in lakes, and the results of published studies are mixed. Studies of the effects of pH on metabolic rates in culture generally indicate a decrease in respiration with decreasing pH (Traaen 1980, McKeown et al. 1968). Traaen (1980) however, found that the lag phase observed in degradation of simple substrates (glucose and glutamic acid) disappeared at pH values down to 4.0 when the microbial seed used in his studies was acclimated at the treatment pH, even though respiration rates in the exponential growth phase were still somewhat lower at pH 4 than at pH 7. Lower pH seems to have a greater effect on the decomposition of more complex substrates, such as tree leaves containing lignin and cellulose, than on simple substrates (Traaen 1980, Leivestad et al. 1976). This occurs for two reasons. First, a relatively small number of organisms can use cellulose, lignin, and other complex substrates, and many of these organisms are pH-sensitive. Second, the microbial degradation of leaves and other structurally complex material in aquatic systems is facilitated by macroinvertibrates and insects that scrape and shred the coarse material, making it amenable to microbial attack. There is good evidence that adverse effects of low pH on these organisms inhibits degradation of leaves and woody material at low pH (Traaen 1980, Hall et al. 1980).

Decomposition at the sediment surface of lakes may be relatively unaffected by increased acidity of the overlying water. Gahnstrom et al. (1980) found little correlation between lake pH and sediment oxygen uptake by 10 cores from seven Swedish lakes (pH 4.5-6.8), although lime treatment of L. Hogsjon (from pH 4.7 to pH 6.6) increased sediment respiration by ~30%. Andersson et al. (1978) found that differences in oxygen consumption or CO_2 production between acidified (pH 3.1) and control (pH 4.5) cores disappeared after 75 days, although glucose turnover times were still longer in the acidified cores. Both Andersson et al. (1978) and Gahnstrom et al. (1980) hypothesized that the amelioration of pH effects on benthic respiration results from neutralization effects of the sediments. For example, Andersson et al. (1978) found that while the difference in pH of the overlying water in the acidified and control cores was 1.5 units, the difference in sediment pH (2 cm depth) was only 0.5 units after the 75 day incubation period. Decreased pH also may affect in-lake decomposition through indirect mechanisms. Gahnstrom et al. (1980) postulated that changes in the rate of sedimentation of organic material may alter sediment respiration rates, and Grahn et al. (1974) suggested that Sphagnum mats which often grow in acidic lakes may inhibit diffusion across the sediment-water interface. It is also plausible that the increased compaction that seems to accompany acidification of sediments (observed in the sediment titration experiments) may result in diminished diffusion.

Whole lake manipulations indicate that decomposition and nutrient cycling are not greatly affected by moderate pH alterations. Schindler et al. (1980) found no changes in levels of dissolved

inorganic carbon or in nutrient levels in Lake 223 following acidification to pH 5.1 and concluded that evidence for reduced decomposition was lacking. Schindler et al. (1980) noted, however, that Lake 223 lacked the coarse particulate shredders that may be most affected by increased acidity. Dillon et al. (1979) found no change in the organic content of the sediments or in aqueous phosphorus concentrations of three Ontario lakes that were limed to raise their pH levels from 4-5 to 7-8. Huitberg and Andersson (1992) reported no change in phosphorus concentrations in three Swedish lakes that had been limed over a period of seven years.

Effects of Low pH on Nitrogen Cycling

The effects of acidification on rates of nutrient cycling in aquatic systems have received very little attention, and the little work that has been done has dealt almost exclusively with phosphorus. Effects of acidification on the nitrogen cycle have been studied in acidic soils and peat bogs, and these studies provide a basis for generating hypotheses on the effects of acidification on nitrogen cycling in aquatic systems.

Ammonification

Other than the brief study by Leivestad et al. (1976), which reported that ammonification of peptone in culture was inhibited below pH 6, there appear to be no studies of pH effects on ammonification in aquatic systems. Alexander (1980) postulated that ammonification would not show marked pH sensitivity because a wide variety of bacteria and fungi can carry out the process. The study of ammonification is complicated by the fact that NH_4^+ can be adsorbed by soils and

sediments and can be converted to nitrate or be reassimilated. For example, Francis (1981) observed greater NH_4^+ accumulation in a pH 4.6 soil than in the same soil that had been acidified to pH 2.6 or neutralized to pH 7.0. Nitrate production, however, was greater in both the acidified and the neutralized soil.

Nitrification

The growth of autotrophic nitrifiers (Nitrosomonas and Nitrobacter) is inhibited in culture below pH 5 (NAS 1978). Although Alexander (1980) also concluded that nitrification in soils is generally inhibited below pH 5, Lee and Stewart (1978) reviewed numerous reports of nitrification in acidic soils and concluded that soil acidity per se does not result in cessation of nitrification. The variability of pH effects on nitrification is illustrated by the study of Klein et al. (1982), who recently examined nitrification rates in acidic (pH 3.6-4.1) soils from the Adirondacks by adding simulated rain (pH 3.6, 4.1, and 5.6) to lab columns. While pH 3.6 rainfall inhibited nitrification in two soils, it stimulated nitrification in the third. Although rates of nitrification varied among treatments, nitrification occurred in all soils and at all rainfall pH levels. In a separate experiment, NH_4^+ additions to flasks containing these soils failed to stimulate NO_3^- production, leading these authors to postulate that heterotrophic nitrification, in which organic N is converted directly to NO_3^-, may have been responsible for the observed nitrification.

Denitrification

Several studies have reported that denitrification rates decrease below pH 7-8 (Nommik 1956, Focht 1974) and that the end product shifts

from N_2 to N_2O (Focht 1974, Blackmer and Bremner 1978). However, as with nitrification, denitrification has also been reported in acidic soils and bogs (Ekpete and Cornfield 1965, Martin and Holding 1978). At low pH chemodenitrification may occur by autodecomposition of NO_2 and by reactions of NO with aromatic compounds (Broadbent and Clark 1965, Bremner and Nelson 1968). The significance of these reactions in natural soils and lake sediments is unknown.

Nitrogen fixation

The most important agents of nitrogen fixation in aquatic systems are blue-green algae. Numerous studies have shown that populations of blue-green algae are reduced at pH levels below 5 (Brock 1973, Leivestad et al. 1976, Almer et al. 1978, Yan and Stokes 1978), and it is reasonable to conclude that nitrogen fixation is also diminished below pH 5. Heterotrophic (bacterial) nitrogen fixation may occur in lakes under anaerobic conditions (MacGregor and Keeney 1973, Brezonik and Harper 1969), and the effects of pH on these organisms has not been studied. However, nitrogen fixation rates appear to be inversely related to inorganic N:P ratios (Vanderhoef et al. 1974) and the softwater lakes that are susceptible to acidification tend to have high N:P ratios. Consequently, nitrogen fixation is not likely to be an important process in these lakes, regardless of pH.

Methods

Littoral Mesocosms

Three in-lake mesocosms (cylindrical enclosures) were placed in the littoral zone of McCloud Lake to evaluate the effects of pH on biological and chemical processes. The 4- m diameter enclosures,

designed after Landers (1979), were placed in the lake in March, 1981 at a depth of one meter. Following a month of stabilization, acid (0.72 N H_2SO_4) was added to lower the pH of one enclosure to 3.6 while base was added to a second enclosure to raise its pH to 5.6. A third enclosure received no acid or base and served as a control. Weekly additions of acid or base were made in an attempt to reach target pH levels within one month. While the low pH was attained within a month, frequent additions of acid were required to maintain a pH of 3.6. The pH of the neutralized enclosure barely changed within the first month, and repeated additions of base were required to maintain a pH of approximately 5. The process of sediment neutralization believed to be responsible for the observed resistance to pH alteration has been discussed in Chapter 3. Throughout the first 16 weeks of the experiment, samples were collected weekly from each mesocosm and from the adjacent littoral water for analyses of pH, major ions, and major nutrients (N and P species). Dissolved oxygen (D.O.) and temperature were measured in the field with a YSI D.O. meter. Chemical analytical methods are described in Chapter 2, methods for sampling and analyses of bacteria, zooplankton, phytoplankton, and chlorophyll are described by Crisman et al. (1983).

During late July and August, 1981, three experiments were conducted to measure diurnal fluxes of O_2, NH_4^+, and soluble reactive phosphate (SRP) across the sediment-water interface of each mesocosm. Clear plexiglass chambers (30 x 20 x 20 cm) were placed on the bottom of each mesocosm and sealed by inserting the bottom edge ~5 cm into the sediment. A pumping system (Figure 5-1) was used to withdraw samples for measurements of D.O. (by Winkler titration in experiment

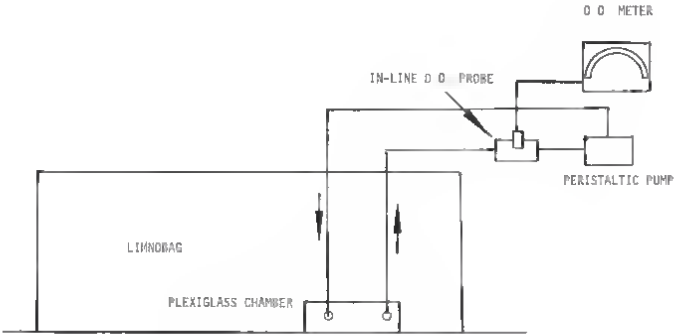


Figure 5-1. Apparatus for sediment flux studies.

1) or to circulate water across an in-line D.O. electrode (experiments 2 and 3). In all three experiments samples were withdrawn for nutrient analyses during each 2-5 hour interval. In the second and third experiments, D.O. and nutrient analyses were also made in the main water column of each mesocosm in order to determine whole-mesocosm fluxes.

Gross productivity, respiration, and net productivity were calculated from diurnal O_2 flux curves using the procedure outlined by Hall and Moll (1978). Ammonium and phosphate fluxes were obtained by integrating the area under the time-flux curves.

Microcosm Experiments

Water-only and sediment-water microcosm experiments were conducted to evaluate decomposition and nitrogen cycling under more controlled conditions. Water-only microcosms were constructed by filling BOD bottles with McCloud lakewater and dried, homogenized substrate (plankton tow material or benthic macrophyte tissue). After pH adjustment (with H_2SO_4 or NaOH) and the addition of a microbial seed, five bottles at each pH level (2.6, 3.6, 4.6, 5.6, and 6.6) were sealed and incubated for three weeks. Dissolved oxygen measurements were made each week using a stirring D.O. electrode and at the end of the incubation period using a Winkler titration. Samples for nutrient analyses (NH_4^+ and SRP) were also collected at the end of the experiment. The three mL of water removed from each bottle for nutrient analyses was replaced with DDW prior to oxygen analysis. The microbial seed in the first experiment was prepared by adding 10 mL sediment + 10 mL lakewater to large test tubes and adjusting the pH of the

water to treatment pH levels. After a one-week acclimation period, 1 mL of overlying water was withdrawn and added to each BOD bottle. The same procedure was used in the second experiment, except that 1 mL activated sludge from a neutral-pH environment was added to the test tubes containing sediment and water prior to pH adjustment.

Nitrogen regeneration was also evaluated in sediment-water microcosms that contained one liter of littoral sediment and nine liters of synthetic lakewater. Following a one-week stabilization period, the pH in all microcosms was 5.8-6.1. Treatment pH levels (3.5, 4.0, 4.5, 5.0, and control-~5.6) were attained by adding acid (1 N H_2SO_4) to duplicate microcosms. Repeated additions of acid were required over the 15-week experiment to maintain desired pH levels, apparently because of neutralization of the added acid by the sediments (see Chapter 3). To measure mineralization products directly, ^{15}N-labelled algae was added to each microcosm. To obtain the labelled algae, Mougeotia sp. was grown on WC medium with $^{15}KNO_3$ substituted for 50% of the $NaNO_3$. The dense growth obtained in three weeks was collected by passing the entire contents of the culture aquaria through 200 u Nitex screen, then through 22 u Nitex screen. The collected algae was then homogenized using the pulse cycle on a Waring blender. The resulting slurry was divided into five beakers and adjusted to treatment pH levels with 0.1 N H_2SO_4. Three fifty mL aliquots from each pH level were poured into smaller beakers and allowed to sit overnight. The last step was taken to assure that any nutrient release due to the shock of rapid pH change would occur prior to adding the algae to the microcosms. Individual aliquots of the algae were then reconcentrated with the Nitex screen and added directly to the microcosms, one beaker

of algal concentrate at each pH level also was saved to determine dry weights. The microcosms were kept in the dark to observe nutrient regeration rates, samples for nutrient analyses and isotope ratio analysis were collected throughout the next 105 days.

Nitrogen Mass Balance

A mass balance of nitrogen in McCloud Lake was compiled for 1992. Methods for measuring wet precipitation and seepage fluxes and for estimating dry deposition of NH_4^+, NO_3^-, NO_2, and HNO_3 were described in Chapter 4. Atmospheric deposition of organic nitrogen was estimated using ratios of organic N/inorganic N observed at other north Florida sites (Grezenik et al. 1993b) together with inorganic N deposition data for the McCloud site.

Results

Enclosure Experiment

Concentrations of nitrogen species in the littoral mesocosms are plotted in Figure 5-2. The most striking observation in this experiment is the large peak in NO_3^- that followed a peak in NH_4^+ in the acidified mesocosm. The increase in NH_4^+ occurred during the seventh through tenth weeks and was accompanied by a decrease in D.O. to <75% saturation (compared with ~ 100% saturation throughout the rest of the experiment). Visual signs of decomposition including increased turbidity (week 10) and floating macrophyte strands and insect castes (week 11) were also observed. Ammonium concentrations peaked at 0.180 mg N/L during week 10 and then declined during the next three weeks while NO_3^- rose to 0.212 mg N/L by week 13. This sequence of events strongly suggests a classic ammonification-nitrification sequence, and

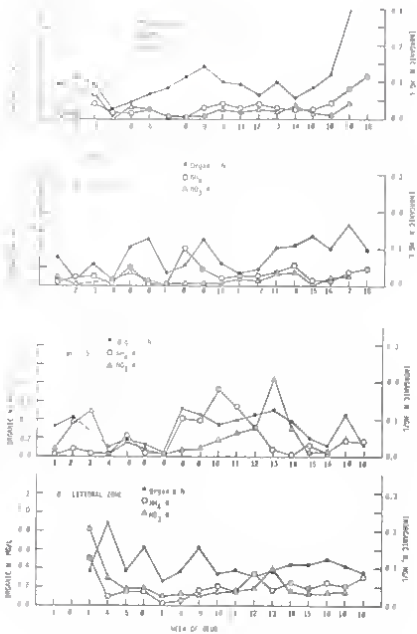


Figure 6-2. Concentrations of organic nitrogen, nitrate, and ammonium in McCloud Lake littoral mesocosms and adjacent littoral zone

is notable because nitrification often is considered to be inhibited below pH 5 (see discussion above).

Levels of inorganic nitrogen were relatively stable in the other mesocosms. Nitrate concentrations increased briefly following the initial addition of base to the neutralized mesocosm but then declined and remained relatively constant. Ammonium concentrations in the control mesocosm showed a moderate increase during weeks 7-8, when algal strands appeared white and were apparently decomposing. Relatively stable inorganic N levels in the two less acidic mesocosms and in the littoral water suggest that nutrients released during mineralization were reassimilated rapidly and did not accumulate. Alternatively, the accumulation of NH_4^+ at low pH may have been the result of decreased NH_4^+ adsorption by the surface sediments.

Differences in levels of total organic nitrogen (TON), NH_4^+, and NO_3^- in the mesocosms and the littoral zone were compared during weeks 5 through 20 using a paired t-test (Mendenhall and Ott 1972). Average levels of TON were similar in all three mesocosms (0.363, 0.343, and 0.304 mg N/L at pH 5, 4.6, and 3.6, respectively), but they were somewhat lower than TON levels in the adjacent littoral zone (mean= 0.420 mg N/L). The mean differences were significant for littoral versus pH 4.5 ($p = 0.02$) and littoral versus pH 3.6 ($p = 0.09$). The most likely explanation for lower TON levels in the mesocosms is decreased turbulence, which reduced the amount of suspended material in the water column. Ammonium concentrations were highest in the pH 3.6 mesocosm (mean = 0.061 mg N/L), largely because of the decomposition event discussed above. The paired t-test shows significant differences in NH_4^+ concentrations between pH 5 and pH 3.6 ($p=0.07$) and

between the littoral zone and pH 3.6 ($p<0.01$). Nitrate levels were also highest in the low pH mesocosm (mean = 0.056 mg N/L) but were similar in the other mesocosms (mean = 0.010 mg N/L at pH 5 and 0.012 mg N/L at pH 4.6) and in the littoral zone (mean = 0.019 mg N/L). Differences between nitrate levels in the acidic mesocosm and the other treatments and the littoral zone were all significant at the 0.10 level or better (Table 5-1).

Measurements of oxygen and nutrient fluxes at the sediment surface revealed distinct diurnal cycles for D.O. and NH_4^+ (Figure 5-3), but SRP concentrations remained so low in the sediment chambers that flux rates could not be determined. During all three 24-hour experiments O_2 levels increased during the day as the result of photosynthesis and decreased during the night when only respiration occurred. Ammonium fluxes were opposite NH_4^+ fluxes were negative during the day (i.e., net removal from the water) and positive at night (i.e., net gain by the water). Presumably this pattern occurred because NH_4^+ assimilation by macrophytes and periphyton was higher during the daytime (Toetz 1971), resulting in a net loss of NH_4^+ from the overlying water. At night, reduced rates of NH_4^+ assimilation in conjunction with continued mineralization of organic nitrogen resulted in positive NH_4^+ fluxes.

Daily respiration in the chambers was computed by connecting the last pre-dawn measurement with the first post-sunset measurement, as suggested by Hall and Moll (1975). The rationale for this is that respiration rates increase during the daytime, as evidenced by the fact that post-sunset respiration rates are nearly always higher than

Table 5-1 Statistical analysis of differences in nitrogen species in littoral mesocosms during 12 weeks following pH adjustment

	Treatment pH pairs [a]					
	5 vs 4.6	5 vs 3.6	4.6 vs 3.6	L vs 5.6	L vs 4.6	L vs 3.6
Organic N						
$\bar{d}$	0.019	0.059	0.040	-0.057	-0.076	-0.116
S_d	0.191	0.167	0.244	0.135	0.097	0.209
t_d	0.34	1.22	0.57	-1.43	2.71	1.92
P	>0.10	>0.10	>0.10	>0.10	0.02	0.09
NH_4^+						
$\bar{d}$	-0.007	-0.034	-0.027	-0.016	-0.010	-0.018
S_d	0.036	0.057	0.068	0.018	0.038	0.063
t	-0.64	-2.07	-1.61	-4.26	-0.91	-0.99
P	>0.10	0.10	0.07	<0.01	>0.10	>0.10
NO_3^-						
$\bar{d}$	0.003	-0.030	-0.032	-0.021	-0.024	0.009
S_d	0.009	0.054	0.051	0.020	0.016	0.039
t	1.12	1.92	2.17	3.64	5.30	0.80
P	>0.10	0.09	0.05	<0.01	<0.01	>0.10

[a] All concentrations in mg/L. $\bar{d}$ = mean difference, S_d = standard deviation, t_d = test statistic for paired t-test, P = probability level

pre-dawn rates. Areas representing respiration (R) and gross primary productivity (GP) are illustrated in Figure 5-3. Net primary production (NP) was calculated as the difference between GP and R. Positive and negative NH_4^+ fluxes were calculated by simply integrating the areas above and below the baseline (Figure 5-1).

Respiration rates in the three experiments (Table 5-2) averaged 1.37, 1.29 and 1.05 g/m^2-d at pH 5, 4.6, and 3.6, respectively, and did not differ significantly among treatments (based on paired t-tests). Mean gross production was nearly identical at pH 5 (1.30 g/m^2-d) and at pH 4.6 (1.29 g/m^3-d) but was slightly lower at pH 3.6 (1.05 g/m^2-d). The paired t-test showed that differences between treatments were marginally significant for pH 3.6 versus pH 4.6 ($p = 0.10$). Net production rates were very low in all chambers and represented a small portion of the daily gross production. Ratios of gross photosynthesis to respiration (P/R ratio) were close to 1.0 during all observations except one (August 25, pH 5). These data indicate that photosynthesis and respiration were essentially balanced at all pH levels during these experiments.

Respiration rates determined in the mesocosm sediments were compared with sediment respiration rates determined for other oligotrophic lakes (Gundersson et al 1980, Andersson et al. 1978, Hayes and MacAuley 1959) to elucidate the relationship between pH and sediment respiration. The data in Table 5-3 include the only two lakes from the study of Hayes and MacAuley (1958) that could be considered clear and oligotrophic (based on data from Hayes and Anthony 1958). The data of Andersson et al. (1978) include sediment respiration rates determined for acidified and non-acidified cores from L. Tjernesjon

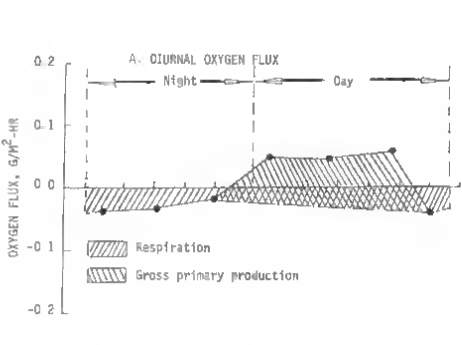


Figure 5-3 Benthic diurnal fluxes of oxygen and ammonium in the acidified mesocosm, August 24-25, 1981.

Table 5-2. Oxygen and ammonium fluxes in littoral mesocosms.

O_2 Fluxes, g/m^2-d

		Sediment				Whole Mesocosm			
Date	pH	GP	R	NP	P/R	GP	R	NP	P/R
7/25	6	1.80	1.73	0.07	1.04	-	-	-	-
	4.6	1.29	1.13	0.10	1.08	-	-	-	-
	3.6	0.94	0.82	0.12	1.15	-	-	-	-
8/10	6	1.66	1.74	-0.08	0.95	3.36	3.62	-0.26	0.93
	4.6	1.35	1.43	-0.08	0.94	4.74	5.54	-0.80	0.86
	3.6	1.09	0.97	0.12	1.12	2.51	2.19	0.32	1.15
8/25	5	0.43	0.65	-0.22	0.66	2.97	3.18	-0.21	0.93
	4.6	1.20	1.27	-0.07	0.94	2.58	3.51	-0.53	0.85
	3.6	1.12	1.24	-0.12	0.90	2.35	2.67	-0.32	0.88

NH_4 Fluxes, mg/m^2 d

		Sediment			Whole Mesocosm		
Date	pH	+	-	Net	+	-	Net
7/25	5	25.2	15.6	9.6			
	4.6	8.0	11.7	-3.7			
	3.6	6.6	10.9	-4.3			
8/10	5	24.4	11.7	12.7	105.6	52.5	53.2
	4.6	17.3	10.6	6.7	32.5	63.3	-30.7
	3.6	10.3	14.2	-3.9	32.7	36.8	-4.1
8/25	5	14.8	1.3	13.5	26.7	11.7	15.0
	4.6	4.7	5.6	-0.8	10.0	8.8	1.2
	3.6	4.8	6.2	-1.4	9.6	8.7	0.9

Table 6-3 DO uptake rates for oligotrophic lake sediments

Lake	pH	Depth	T, °C	O_2 g/m^2-d	O_2 at 20 °C[a]
Bluff, Hayes & MacAuley (1959)	6.3		11	188	0.393
Grand, Hayes & MacAuley (1959)	6.4		11	264	0.552
L. Gardsjon Gahnstrom et al (1980) (3/79)	4.5	3	6	305	0.562
	4.6	18	6	411	1.296
(11/78)	4.5	3	7	312	0.81
	4.6	18	7	569	1.65
L. Fiolen (2/77) Gahnstrom et al (1980)	6.5	8	5	401	1.37
L. Hogsjon (10/77) Gahnstrom et al. (1980)	4.7	15	10	470	1.07
L. Tjarnesjon (6/76) Gahnstrom et al (1980)	5.0	25	10	439	1.00
L. Stora Needen (6/76) Gahnstrom et al (1980)	5.1	48	10	257	0.58
L. Stora Hästevatten (6/79) Gahnstrom et al (1980)	5.2	8	12	411	0.79
L. Skarsjon (6/76) Gahnstrom et al. (1980)	5.2	8	12	377	0.73
L. Tjarnesjon, Andersson et al. (1978)	4.5	-	10	552	1.18
	3.1	-	10	552	1.18
McCloud Lake mesocosms					
pH 5 7/25	4.8	1	30	1.73	0.76
8/10	4.6	1	31	1.74	0.83
8/26	4.6	1	31	0.65	0.31
pH 4.6 7/20	4.5	1	30	1.19	0.52
8/10	4.4	1	31	1.42	0.68
8/25	4.4	1	31	1.27	0.61
pH 3.6 7/20	3.7	1	30	0.82	0.39
8/10	3.8		31	0.97	0.46
8/25	3.7		31	1.24	0.59

[a]See equation 6-1

following a 75 day acclimation period. Since sediment respiration rates were determined at a variety of temperatures in these studies, the published rates were converted to respiration rates at 20° using the equation (Metcalf and Eddy, 1972):

$$K_2 = K_1 \exp^{t_c(T_1 - T_2)} \qquad (5\text{-}1)$$

where K_1, K_2 = respiration rates at temperatures T_1 and T_2 respectively, and
t_c = temperature correction factor.

The value used for t_c in these calculations was based on a review of literature on factors affecting benthic respiration (Baker 1980) and corresponds to a Q_{10} of 2.23. Figure 5-4 shows that there is little relationship between pH and respiration for the lakes studied, a straight-line linear regression for these data has a correlation coefficient of only 0.05. These data suggest that pH does not greatly affect sediment oxygen consumption in lakes.

Whole mesocosm GP and R, determined on August 10 and August 24 (Ogburn, unpublished data) show no differences in GP or R among treatments (Table 5-2). It is interesting to note that benthic GP and R generally were less than 50% of the whole mesocosm GP and R, even though the depth of the mesocosms at the time of these experiments was less than 1 m. These data suggest that phytoplankton and the periphyton and associated fauna attached to the polyethylene limnobags contributed substantially to the metabolism of the mesocosms. There was no discernible pH trend in the ratio of sediment/whole mesocosm GP or R.

Benthic ammonium fluxes showed a clear pH trend. Positive fluxes of NH_4^+ were greater at pH 5 (mean = 22 mg/m^2-d) than at pH 4.6 (mean

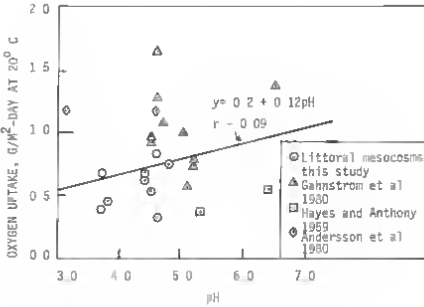


Figure 5-4. Sediment oxygen utilization at 20° C

10 mg/m^2-d) or pH 3.6 (mean = 7 mg/m^2-d). The paired t-test indicates that the differences were significant between pH 5.6 and pH 4.6 ($p = 0.07$) and between pH 5 and pH 3.6 ($p = 0.03$). Negative NH_4^+ fluxes were similar in all three mesocosms and generally lower than the positive fluxes (Table 5-2). Net NH_4^+ fluxes were positive at pH 5 (mean = 12 mg/m^2-d) and at pH 4.6 (mean = 0.7 mg/m^2-d) but negative at pH 3.6 (mean = -3.2 mg/m^2-d). These differences were significant for pH 5 versus pH 4.6 ($p = 0.05$) and for pH 5.6 versus pH 3.6 ($p < 0.01$). Positive fluxes for the whole mesocosms also were higher at pH 5 (65 mg/m^2-d) than at pH 4.6 or pH 3.6 (mean = 21 mg/m^2-d in each), while negative fluxes were relatively uniform (Table 5-2). These differences were, however, not significant at the $p = 0.10$ level.

Ammonium Adsorption

Effects of acidification on phosphorus adsorption and precipitation have been studied (Almer et al. 1978), but there is no mention in the literature on the effects of acidification on NH_4^+ adsorption. It is reasonable to postulate that NH_4^+ is desorbed from sediment surfaces at low pH because surfaces are less negatively charged at low pH. To determine whether desorption occurs, NH_4^+ levels were measured at each pH level of a batch acidification experiment (Chapter 3) using McCloud littoral sediment. The results (Figure 5-5) show that NH_4^+ desorption is substantial below pH 5. At pH 4.84 (control), the average ammonium concentration was 0.033 mg N/L, and the concentration increased to 0.140 mg N/L at pH 3.57. Since biological activity was inhibited by the the addition of chloroform, cation exchange is the only reasonable mechanism to account for these results. It can be inferred from these results that lake acidification may result in

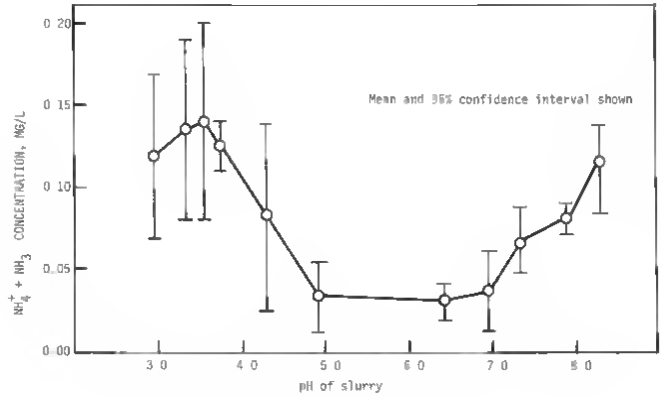


Figure 5-5 Ammonium adsorption in McCloud Lake littoral sediment batch study

enhanced NH_4^+ release if the pH of the surficial sediments also decreased.

As pH levels approach the pK_A for NH_4^+ (≈8.3), an increasing fraction of the total NH_3 + NH_4^+ is present as NH_3, a neutral species that does not undergo cation exchange. At pH 7, only 5% of the total NH_4^+ + NH_3 exists as NH_3, while at pH ≈8.3, 50% exists as the non-ionized species that would be found in solution rather than on sediment surfaces. Thus, as pH in the experimental bottles increased from 5.0 to 8.0, ammonium levels increased from less than 0.05 mg N/L to over 0.12 mg N/L (Figure 5-5).

Microcosm Experiments

Water-only microcosms

In the initial decomposition experiment, pH-adjusted McCloud sediment was used as seed to facilitate microbial decomposition of dried plankton. Measurements of dissolved oxygen at the the end of week 3 show that maximum O_2 uptake occurred at pH 4.5. Uptake was significantly lower at pH 2.6 and at pH 6.6 (Figure 5-6A). Apparently, the one-week acclimation period was not sufficient to grow bacteria with higher pH optima. The experiment was repeated using a mixed seed developed from McCloud sediment and activated sludge (pH ~7). The results of this experiment (Figure 5-6B) show that O_2 uptake increased in the pH range 2.6 to 4.6 but remained constant in the pH range 4.6 to 6.6. The addition of bacteria from a neutral-pH environment (activated sludge) thus broadened the pH range of optimum oxygen uptake, presumably reflecting the mixture of bacteria having different

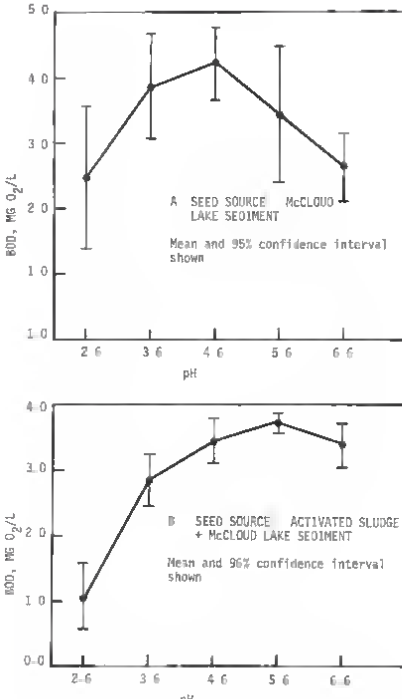


Figure 5-6 Three week BOD versus pH with McCloud Lake sediment seed (A), and activated sludge + sediment seed (B)

pH optima. The results suggest that bacteria from the surficial sediment of McCloud Lake are well-adapted to their environmental pH.

Sediment-water microcosms

Ammonium concentrations in the sediment-water microcosms fluctuated considerably (Figures 5-7 to 5-11) but did not increase significantly following the addition of labelled algae in any of the microcosms with a pH > 4. At pH 3.5, a modest rise in NH_4^+ levels did occur (Figure 5-7). Concentrations in both pH 3.5 aquaria increased to ~ 0.140 mg N/L by day 17, then gradually declined. Isotope ratio analyses of microcosm NH_4^+ conducted on days 2, 9, 22, and 38 showed that very little of the NH_4^+ in the water at any time originated from the labelled algae (Table 5-4). The maximum observed $^{15}NH_4^+$ concentrations in the microcosms were at pH 3.5 (0.010 mg $^{15}N/L$ in replicate A and 0.014 mg $^{15}N/L$ in replicate B), $^{15}NH_4^+$ levels in the other microcosms never exceeded 0.010 mg/L. Since the 68 mg algae added to each microcosm with a 50% label contributed ~0.18 mg organic N/L, the NH_4^+ in the water column always was less than 8% of the organic N added. These results are consistent with those of Nichols and Keeney (1973) who reported little ammonium release following the addition of herbicide-killed macrophytes to sediment-water microcosms.

Thus, most of the increase in NH_4^+ at pH 3.5 was apparently due to the continued release of sediment-bound NH_4^+. As noted earlier, frequent additions of acid were required to maintain the low pH levels in this experiment, and the release of sediment-bound NH_4^+ continued during at least the first 30 days following the addition of labelled algae. These results are consistent with the finding of NH_4^+ desorption in the sediment acidification experiments.

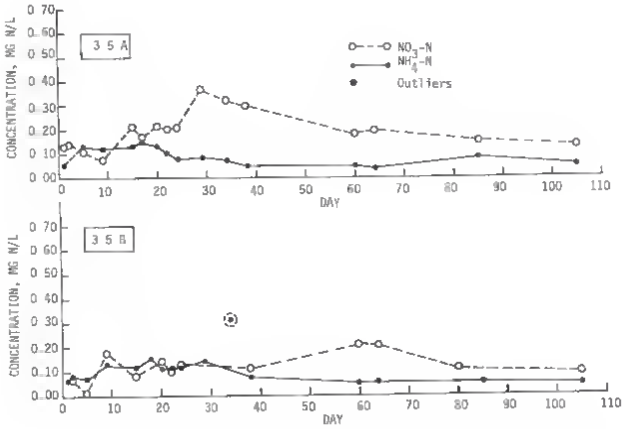


Figure 5-7 Ammonium and nitrate concentrations in pH 3 6 sediment-water microcosms

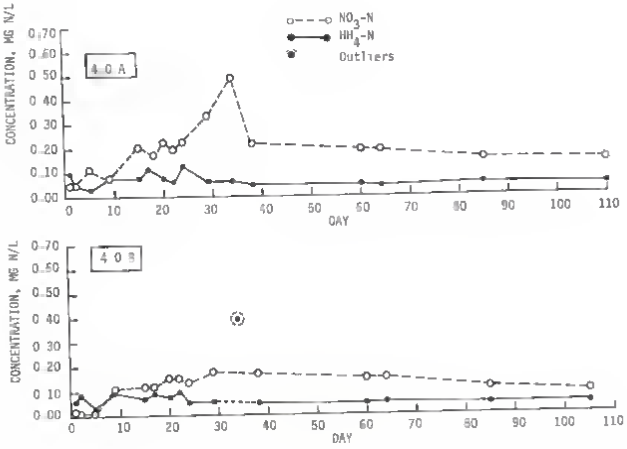


Figure 5-8. Ammonium and nitrate concentrations in pH 4.0 sediment-water microcosms

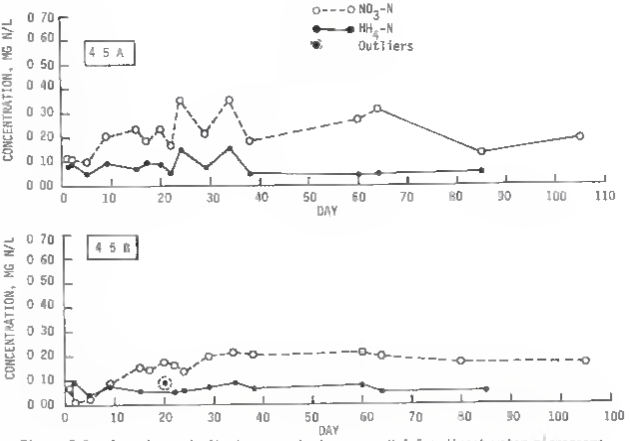


Figure 5-9 Ammonium and nitrate concentrations in pH 4 5 sediment-water microcosms

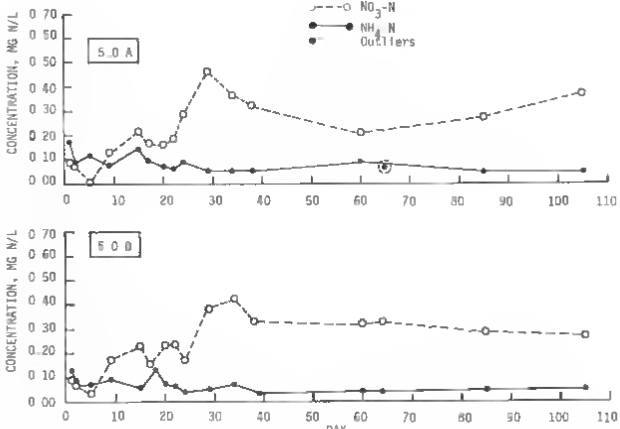


Figure 5-10 Ammonium and nitrate concentrations in pH 5.0 sediment-water microcosms

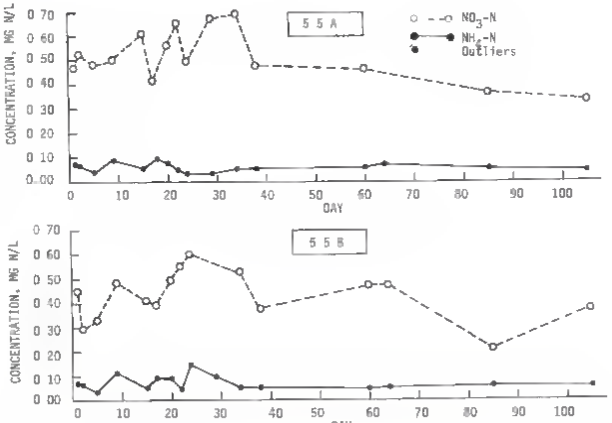


Figure 5-11. Ammonium and nitrate concentrations in pH 5 5 sediment-water microcosms

Table 5 4. Concentrations of $^{15}NH_4$-N in sediment-water microcosms

pH and Replicate	Values in mg N/L			
	Day 2	Day 9	Day 22	Day 38
3.5 A	-	0.009	0 010	0 002
3 5 B	<0.001	0.014	0.010	0 005
4.0 A	<0 001	0.005	0.002	<0.001
4 0 B	<0.001	0 009	0 001	<0.001
4 5 A	<0 001	0.005	0 001	<0 001
4 5 B	<0.001	0.003	<0.003	<0.001
5 0 A	<0 001	0 003	0 002	<0 001
5 0 B	<0 001	0 003	0 002	0 002
5 5 A	<0.001	0.003	0.001	<0.001
5 5 B	<0 001	0 003	0 001	<0.001

Levels of NO_3^- increased in all microcosms. Since no nitrate was added, and NO_3^- does not accumulate in sediments by adsorption, it is clear that nitrification occurred at all pH levels. At pH 3.5, NO_3^- levels increased from 0.123 mg N/L at day 1 to 0.369 mg N/L by day 29 in replicate A and from 0.063 mg N/L at day 1 to 0.210 mg N/L by day 50 in replicate B. Although nitrate levels increased significantly at pH 3.5 and 4.0, the increases were more pronounced at pH 5, where concentrations increased from < 0.100 mg N/L to over 0.400 mg N/L within the first month (Figure 5-10). At pH 5.7 (control), NO_3^- levels were already high (~0.45 mg N/L) when the labelled algae were added, but increased further to over 0.60 mg N/L within the first month (Figure 5-12).

Isotope ratio analyses were not conducted for the NO_3^- in the microcosms, and consequently it is not possible to determine the fraction of NO_3^- produced that originated from the labelled algae. It is likely that some of the NO_3^- originated from sediment-bound NH_4^+ that was oxidized following release to the water. Regardless of the ammonium source, it is clear that nitrate was produced, even at pH 3.5. This confirms the observation of nitrification in the McCloud Lake littoral mesocosms and demonstrates that nitrification can occur in highly acidic lakes. Further work is needed to demonstrate whether the process is mediated by pH-tolerant heterotrophs or whether autotrophic nitrifiers carry out the process in relatively neutral sediments.

McCloud Lake Nitrogen Balance

Precipitation

Methods of measuring inorganic nitrogen deposition were discussed in Chapter 3. To estimate the input of total nitrogen entering McCloud Lake, an estimate of organic N was needed. Brezonik et al. (1983b) reported that organic N deposition in bulk precipitation was 36-64% of the inorganic N deposition at 4 north Florida sites (Gainesville, Waldo, Jasper, and Hastings). These ratios were used to estimate organic N deposition to McCloud Lake from the bulk deposition (wet + aerosol) inorganic N (Table 5-5).

Wet deposition accounted for 20-48% of the total deposition of NO_3^- and NH_4^+. Since concentrations of both inorganic species were inversely correlated with monthly precipitation volume ($r = -0.53$ for NO_3^- and -0.47 for NH_4^+), monthly loadings were fairly uniform (Figure 5-12). Gaseous deposition of NO_2 and HNO_3 (3.1-9.2 kg/ha-yr) was an important source of NO_3^- to the lake, accounting for approximately 40% of the atmospheric nitrogen input. Aerosol NH_4^+ deposition was a minor source of nitrogen, accounting for only 0.1 - 0.3 kg N/ha-yr. Deposition of organic N, estimated to be 1.2-3.6 kg N/ha-yr, was comparable with bulk (wet + dry) ammonium deposition.

Bulk precipitation of total N (Table 5-5) at McCloud Lake (estimated from wet + aerosol deposition to be 4.4 - 9.3 kg/ha-yr) was similar to the state average of 7.7 kg/ha-yr (Brezonik et al. 1983b) and to the 1968 bulk deposition at nearby Anderson-Cne Lake (Brezonik et al. 1969). While bulk total N deposition has not changed appreciably in 14 years, bulk NO_3^- deposition appears to have increased from 1.7 kg/ha-yr to 2.1-3.3 kg/ha-yr.

Table 5-5. Deposition of nitrogenous species at McCloud Lake

	kg/ha-yr			
	NH_4^+	NO_3^-	TON	TN
McCloud Lake, 1982				
Wet only	1.0	2.0		
Aerosol	0.1-1.4	0.1-1.3		
Est. bulk	1.1-2.4	2.1-3.3	1.2-3.6	4.4-9.3
Gaseous	-	2.9-8.7 (NO_2)		
		0.2-0.5 (HNO_3)		
Total	1.1-1.4	5.2-12.5	1.2-3.6	7.5-17.5
Andersen-Cue, 1982				
Bulk	1.7	1.7	2.9[a]	5.3
State ave., 1978-79				
Bulk				7.7

[a]Nine-month total.

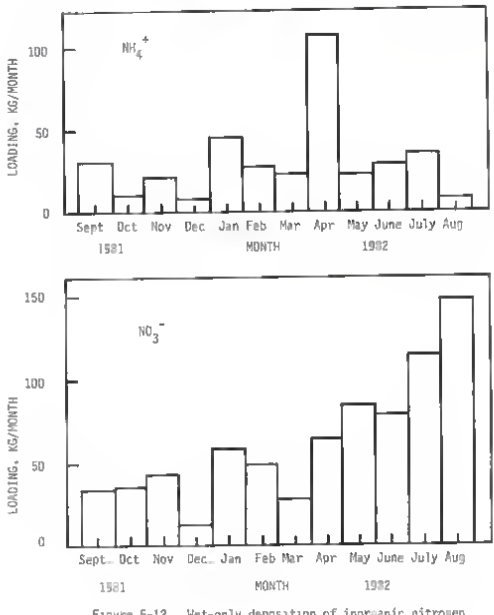


Figure 5-12 Wet-only deposition of inorganic nitrogen to McCloud Lake

McCloud Lake nitrogen

Concentrations of organic N and inorganic species fluctuated considerably during 1981-1982, although a seasonal pattern is not clear (Figure 5-13). The distinct rise in nitrate levels during the fall and winter suggests that nitrification may have occurred, particularly since increasing NO_3^- levels paralleled a decline in NH_4^+. However, NO_3^- deposition during the period October, 1981 -January 1982 was estimated to be 7-20 kg, or 0.06-0.17 mg N/L lakewater, and could account for the observed rise if algal uptake of nitrate were minimal.

Data in Table 5-6 indicate that the TN/TP ratio in 1981-82 was 40:1 while the ratio of soluble inorganic nitrogen to soluble reactive phosphate (SIN:SRP) was 33:1. Since a SIN:OP ratio of 20:1 generally is recognized as an indication of phosphorus limitation (Porcella and Bishop 1975), it can be concluded that algal growth in McCloud Lake is phosphorus limited.

Nutrient data from 1968-69, 1978-79, and 1981-82 (Table 5-6) reveal no significant trends in TON, NH_4^+, NO_3^-, total P, or SRP. If acidification has caused a decreased in nutrient levels, the trend is not yet discernible in McCloud Lake. This observation is consistent with the studies of Schindler et al. (1980), Hultberg and Andersson (1982), and Dillon et al. (1979) which report little or no change in nutrient levels following artificial pH manipulations in lakes.

Mass balance

As noted in Chapter 3, 98-99% of the nitrate and 95-98% of the ammonium entering McCloud Lake comes from atmospheric deposition. Organic nitrogen in seepage was not measured, but since seepage flows

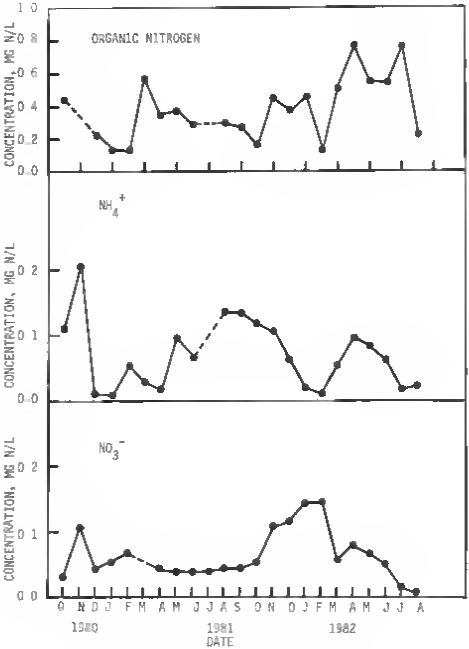


Figure 5-13 McCloud Lake nitrogen species.

Table 6-6 McCloud Lake nutrient concentrations, 1968-1982.

	Concentrations as mg/L		
	1968[a]	1978[b]	1981-82
Total organic N	0.420	0.243	0.363
NH_4^+ - N	0.105	0.184[c]	0.070
NO_3^- - N	0.041		0.063
Total N	0.566	0.427	0.484
Organic P	0.006	0.011	0.012
PO_4^- - P	0.006	0.005	0.004
Total P	0.012	0.016	0.012
TN/TP	47	27	40
SIN/OP	24	37	33

[a] Brezonik et al (1969)

[b] Brezonik et al. (1983b).

[c] Total inorganic nitrogen.

were <10% of the total water input, inputs of organic N via seepage were assumed to be negligible.

Inorganic nitrogen entering the lake was rapidly immobilized. Ammonium has a residence time of 0.7-1.4 years and nitrate has a residence time of 0.1-0.3 years (Table 5-7). Ammonium probably is immobilized by biological assimilation and sedimentation as organic N. Nitrate is immobilized by biological assimilation, but also may be lost via denitrification. Several lines of evidence support the view that denitrification may occur in McCloud Lake. First, nitrate was almost completely removed from the elute in the groundwater seepage experiments (Chapter 3). Second, pore water profiles in both the littoral and profundal sediments (methods described in Chapter 4) show a dramatic NO_3^- gradient in the upper 5 cm (Figure 5-14), suggesting that nitrate diffuses into the surficial sediments and is transformed. Finally, NO_3^- levels in the sediment-water microcosms decreased after reaching peak levels (Figures 5-7 to 5-11). Although these data clearly suggest that nitrate is transformed in the sediments, it is not certain whether denitrification is the mechanism responsible. Assimilation by macrophytes, algae, or bacteria in the surficial sediments could cause the observed depletion of nitrate. However, while denitrification is a pH-sensitive process, other pH-sensitive processes, including sulfate reduction and nitrification, can occur in McCloud Lake sediments. Thus, low pH of the overlying water is not *a priori* evidence that denitrification could not occur. Although these data suggest that denitrification may occur, identification of end products (N_2O or N_2) would be needed to provide conclusive evidence.

Table 5-7 McCloud Lake nitrogen budget

	NO_3^-, Kg N/yr	NH_4^+, Kg N/yr	Organic N, Kg N/yr
Precipitation	26.7-63.6	5.9-12.4	6.0-18.1
Wet	10.4	5.2	
Dry	16.3-53.2	0.7-7.2	
Aerosol	0.7-6.4	0.7-7.2	
Gas	15.6-46.8	-	
Seepage			
In	0.6	0.4	?
Out	1.1	1.2	?
Storage	9.4	8.4	55.9 kg
Δ_S	-4.4	-13.8	
τ, yr	0.1-0.3	0.7-1.4	3.1-5.3

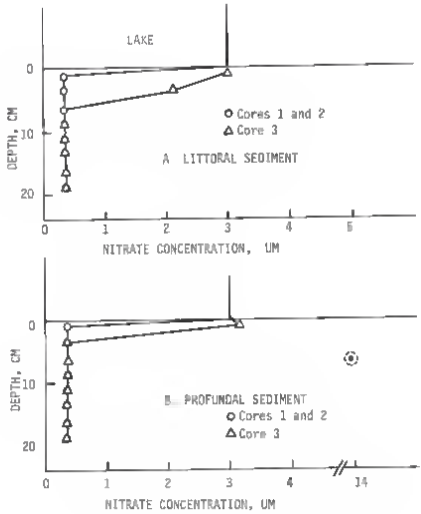


Figure 5-14 Nitrate in McCloud Lake sediment pore waters

It can be seen that organic N in McCloud Lake has a much longer residence time (3.1-9.3 years) than the inorganic species. This undoubtedly occurs because inorganic N is assimilated in the water column, resulting in sustained high levels of organic N.

The significance of atmospheric nutrient loading in maintaining productivity can be seen by comparing atmospheric inputs of N and P to McCloud Lake to established nutrient loading criteria (Vollenweider 1968, 1975, Shannon and Brezonik 1972). Current phosphorus loadings to the lake are approximately one half or less of the loading that would be required to sustain mesotrophic conditions (Table 5-8). Nitrogen loadings, in contrast, are at or near the minimum mesotrophic loading rates. These data support the contention, based on inorganic N/P ratios, that lake productivity is phosphorus limited, and illustrate the significance of atmospheric nutrient deposition as a source of nutrients to seepage lakes in this region. Although this study has focused on the impact of acidification, atmospheric deposition is also significant from a standpoint of eutrophication. Since McCloud Lake receives enough nitrogen through atmospheric deposition to sustain mesotrophic conditions, the addition of small amounts of phosphorus would result in enhanced productivity. For example, according to the Vollenweider (1975) loading criterion, the addition of 0.2 mg P/m^2-yr would result in mesotrophic conditions. For this 5 hectare lake, 0.2 mg P/m^2-yr corresponds to the addition of only 10 kg phosphorus, an input that would occur with the addition of domestic waste from a mere 5 individuals assuming an input of 2 kg/capita-yr (Vollenweider 1968). While McCloud Lake is protected from residential development,

Table 5-8. Atmospheric deposition of nitrogen and phosphorus relative to loading criteria.

Criterion	Units	Minimum mesotrophic loading	McCloud atmospheric input
Phosphorus			
Vollenweider (1968)	g/m^2-yr	0.044	0.027
Shannon & Brezonik (1972)	g/m^3-yr	0.022	0.010
Vollenweider (1975)	g/m^2-yr	0.10-0.11	0.027
Nitrogen			
Vollenweider (1968)	g/m^2-yr	0.67	0.7-1.8
Shannon & Brezonik (1972)	g/m^3-yr	0.86	0.3-0.7

extensive development is occurring on nearby lakes and can be expected to cause enhanced productivity of these lakes. Thus, while atmospheric deposition of acidic nitrogen species may be largely neutralized by incorporation into organic matter, atmospheric nitrogen inputs may contribute to enhanced algal productivity.

Conclusions

Although Grahn et al. (1974) and others have postulated that lake acidification results in diminished nutrient regeneration, this study and other recent studies indicate that the effect of acidification on decomposition and nutrient regeneration may be minimal. Evidence to support this conclusion include the following:

1) There is no demonstrated reduction in sediment oxygen utilization with decreasing pH. There were no significant differences in sediment respiration rates among the littoral mesocosms (pH 3.5-5). Data compiled from other studies also fail to show a pH trend.

2) The water-only microcosms showed that oxygen uptake was higher at pH 4.5 than at higher or lower pH levels when McCloud litoral sediments were used as a seed, indicating that microorganisms in the surficial sediments are adapted to the lake pH.

3) Nitrification, which is often assumed to cease below pH 5, occurred in the littoral mesocosms and in the sediment-water microcosms at a pH of 3.5, although rates appeared to be reduced below pH 4.5-5. Further study is needed to determine whether the process is mediated by autotrophic nitrifiers living in the relatively neutral sediments or whether the process is mediated by pH-tolerant heterotrophs.

4) Denitrification may also occur in McCloud Lake. Nitrate was depleted in *in situ* littoral and profundal sediment pore waters. Over 90% of the nitrate was removed from the eluates in the groundwater seepage experiment, and nitrate levels decreased from peak levels in the microcosm experiment.

5) Concentrations of inorganic and organic nitrogen and phosphorus species in McCloud Lake do not appear to have changed significantly over the past 14 years, despite a decrease in pH of nearly 0.5 units.

The accumulation of NH_4^+ in the acidified littoral mesocosms and in the acidified sediment-water microcosms suggests that some ammonium regeneration occurs at pH levels down to 3.5. This accumulation in the water column may result from decreased NH_4^+ adsorption at low pH (demonstrated in the sediment titration experiments) or because of reduced assimilation or nitrification. The diurnal sediment flux studies show that positive NH_4^+ fluxes decreased with decreasing pH, but is not clear whether this occurred because of decreased ammonification at low pH or because of reduced assimilation by the benthic macrophyte community.

Atmospheric inputs accounted for over 95 % of the total nitrogen input to the lake. Inorganic nitrogen entering McCloud Lake was rapidly immobilized. This is significant because it results in a net consumption of protons in the lake, as discussed in Chapter 3. Atmospheric inputs of nitrate, but not of total nitrogen, appear to have increased somewhat during the past 14 years. Atmospheric nitrogen inputs are currently sufficient to maintain mesotrophic conditions.

CHAPTER 6
CONCLUSIONS

Sediment Neutralization

Laboratory experiments conducted with sediment-water slurries showed that sediments from softwater lakes can neutralize additions of acidity. The acid neutralizing capacity of profundal sediments is as high as 20 meq/100 g in the pH range 4.5-5.5 and is correlated with the organic content of the sediments. Cation exchange is the major abiotic mechanism of H^+-neutralization. Sulfate adsorption, protonation of humic acids, and dissolution of aluminum minerals were unimportant as neutralization mechanisms. Evidence of sulfate reduction was obtained in the seepage column experiments and from *in situ* sediment pore water analyses in McCloud Lake, and this process is probably an important H^+-consuming mechanism in McCloud Lake sediments.

McCloud Lake Mass Balance

McCloud Lake receives 90% of its water from precipitation, the remaining 10% of the inflow is groundwater seepage. Nearly all of the sulfate, nitrate, ammonium, sodium, chloride, and protons in McCloud Lake enter via precipitation. An internal sink (sulfate reduction) consumed 37-73% of the sulfate entering the lake. Approximately 90% of the ammonium and nitrate entering the lake was consumed by internal sinks. Biological assimilation is undoubtedly the most important sink for inorganic nitrogen species. Additional losses of ammonium may

occur by adsorption to sediment surfaces and additional losses of nitrate may occur by denitrification. Most (86-94%) of the protons entering the lake were removed by internal sinks, primarily sulfate reduction and assimilation or denitrification of nitrate.

Nitrogen Cycling and Decomposition

Although decomposition is believed to be retarded in acidic lakes, there was no evidence for reduced sediment oxygen utilization in the littoral mesocosms in the pH range 3.6 to 5. Data compiled from other studies also fail to show a pH trend in sediment oxygen utilization. Water-only microcosms showed that oxygen utilization was highest at pH 4.5 when McCloud Lake sediment was used as a seed, indicating that bacteria in the lake are well-adapted to acidic conditions.

Nitrification, which is often assumed to cease below pH 5, occurred in the littoral mesocosms and in the sediment-water microcosms at pH levels as low as 3.5, although nitrification rates were reduced below pH 4.5-5.0. Nitrification probably occurs in the surficial sediments, where pH levels are higher than lake pH levels. Denitrification, which is also believed to be inhibited below pH 5, occurred in the seepage experiment and in the *in situ* sediments.

Concentrations of nutrient species do not appear to have changed significantly during the past 14 years, although the lake pH has decreased by 0.5 units. This observation is consistent with the results of several whole-lake manipulation experiments and suggests that nutrient levels in lakes may not decrease appreciably with moderate acidification.

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APPENDIX McCLOUD LAKE HYDROLOGIC AND CHEMICAL DATA

Table A-1 McCloud Lake water budget, September, 1981, to August, 1982

Month	Precipitation 10^3 m^3	Evaporation 10^3 m^3	Seepage 10^3 m^3	Volume 10^3 m^3	Change in volume 10^3 m^3	Area 10^3 m^2	Change in area 10^3 m^2
Sept , 1981	1 56	5 01	-2 89	126 01	-2 36	50 30	-0 35
Oct	1 50	4 45	-3 05	123 50	-2 51	49 97	-0 33
Nov.	4 89	2 75	-1 42	123 21	-0 29	49 90	-0 07
Dec	1 28	2 05	-2 14	120 50	-2 71	49 35	-0 55
Jan , 1982	9 24	2 85	-1 55	121 26	0 76	49 70	-0 35
Feb.	4 84	2 85	-0 94	121 26	0 00	49 35	-0 35
March	5 50	4 14	-1 31	117 45	-3 81	48 70	-0 65
April	9 94	5 06	2 12	127 75	10 30	51 23	2 53
May	7 90	6 34	2 31	130 44	2 69	50 97	-0 26
June	12 23	6 35	1 09	134 60	4 15	51 60	0 63
July	7 38	6 28	0 39	143 88	9 28	53 10	1 50
August	8 93	5 73	2 66	148 85	4 97	53 77	0 67

Table A-2. Major ions in McCloud Lake, October, 1980, to August, 1982.

Month[a]	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	SO_4^{2-}	Cl^-
	- All values in ueq/L -						
October, 1980	-	112	66	7.4	126	-	154
November	24.5	118	66	6.9	121	111	150
December	27.0	102	65	9.7	128	-	163
January, 1981	16.7	58	64	6.5	120	-	-
February	78.5	79	66	5.4	114	-	-
March	27.8	47	65	5.6	116	133	- -
April	30.9	48	62	6.4	126	138	-
May	30.8	64	62	9.0	138	152	-
June	28.2	36	66	8.5	136	137	-
July	29.3	-	-	-	-	-	197
August	27.5	-	-	-	-	-	167
September	30.4	64	63	6.4	189	184	167
October	35.2	52	66	6.8	199	231	170
November	38.1	58	63	5.7	179	196	185
December	39.6	50	69	6.5	229	214	189
January, 1982	43.8	48	69	5.2	188	206	174
February	33.2	48	66	4.2	181	207	174
March	28.5	61	65	4.1	166	191	159
April	30.5	53	65	4.7	170	175	155
May	35.6	62	66	4.8	163	210	205
June	25.2	58	68	7.1	147	155	177
July	23.0	56	67	6.9	137	138	137
August	25.1	51	67	7.0	139	159	173

[a]Values represent means of all depths.

Table A-3. Physical data and nutrients in McCloud Lake, October, 1980 to August, 1982.

			- nutrient data in mg/L -				
Month[a]	Conductivity, uS/cm @ 20 °C	Temp., °C	TKN	NH_4^+	NO_3^-	Total phosphorus	Ortho-phosphorus
Oct., 1980	-	-	0.532	0.130	0.031	0.007	0.007
Nov.	52	17.1	0.144	0.021	0.107	0.007	0.006
Dec.	-	-	0.238	0.010	0.039	0.007	0.007
Jan., 1981	53	-	0.160	0.009	0.054	0.007	-
Feb.	-	18.0	0.183	0.053	0.068	0.009	0.003
March	56	21.8	0.502	0.030	-	0.010	0.007
April	-	25.1	0.386	0.016	0.043	0.018	0.006
May	69	27.1	0.480	0.099	0.039	0.007	0.005
June	-	30.2	0.351	0.067	0.037	0.007	0.002
July	-	-	0.326	-	0.040	0.009	0.004
August	-	-	0.485	0.137	0.044	0.010	0.003
Sept.	50	27.0	0.409	0.136	0.044	0.032	0.003
Oct.	-	24.0	0.278	0.119	0.065	0.011	0.003
Nov.	-	18.0	0.537	0.107	0.108	0.011	0.001
Dec.	44	15.0	0.442	0.063	0.118	0.005	0.001
Jan., 1982	47	17.0	0.461	0.020	0.145	0.007	0.001
Feb.	-	21.0	0.140	0.011	0.143	0.001	0.001
March	43	25.0	0.564	0.054	0.058	0.017	0.003
April	41	26.0	0.865	0.098	0.080	0.008	0.001
May	37	24.0	0.637	0.044	0.063	0.031	0.010
June	43	29.0	0.619	0.063	0.051	0.018	0.003
July	42	31.0	0.780	0.019	0.015	0.023	0.004
August	40	32.0	0.281	0.023	0.007	0.011	0.002

[a]Values represent means of all depths.

Table A-4. Chemistry of McCloud Lake wet-only precipitation, May, 1981, to September, 1982.

		- All chemical data in ueq/L -								
Month	Precip. cm/mo.	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	SO_4^{2-}	Cl^-	HO_3^-	HH_4^+
May, '81	2.1	28.6	4.5	1.6	0.90	4.6	23.7	7.5	11.8	13.3
June	17.3	38.2	5.0	4.8	0.50	15.7	32.5	18.9	22.5	16.0
July	9.0	64.4	8.5	3.0	0.90	15.1	79.4	20.1	34.0	27.7
August	12.3	74.8	10.0	4.2	0.30	11.2	63.8	13.5	29.4	13.6
Sept.	3.3	32.4	14.2	4.9	0.70	5.3	61.2	6.3	19.6	18.1
Oct.	3.0	35.5	9.0	7.7	0.80	31.9	43.3	36.7	22.1	7.1
Nov	9.8	23.4	2.5	3.6	0.40	15.7	25.8	17.5	8.6	4.3
Dec.	2.6	24.5	5.0	4.0	0.90	13.1	28.3	14.9	8.6	6.4
Jan., '82	18.6	22.4	3.6	2.1	1.40	12.7	24.0	15.5	6.4	5.0
Feb.	9.8	20.9	4.0	3.5	1.00	23.1	20.0	29.6	10.0	5.7
March	11.3	24.0	2.5	2.7	0.50	12.7	26.7	15.5	5.0	4.3
April	19.4	30.2	7.0	4.5	0.70	10.0	43.6	11.0	6.4	10.7
May	15.5	33.9	1.1	2.6	0.20	7.0	24.8	6.5	10.5	2.8
June	23.7	17.0	2.0	1.5	0.40	5.2	15.6	4.5	6.4	2.4
July	13.9	33.7	3.6	2.2	1.30	10.9	28.5	11.0	15.5	4.9
August	16.6	35.7	3.3	2.4	0.40	7.9	28.1	8.5	16.6	0.9
Sept.	27.6	44.0	5.6	2.6	0.70	9.2	35.5	9.9	22.3	6.6

Table A-5. Chemical composition of in-seepage to McCloud Lake, April, 1982, to September, 1982.

Month[a]	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+
April, '82	0.40	94	47	32	23	31	36	8.7	1.3
May	1.66	72	47	23	11	26	31	2.5	6.4
June	0.71	123	67	43	18	41	39	3.2	1.8
July	1.30	48	34	19	22	18	26	4.6	4.2
August	0.88	93	64	53	27	52	57	2.1	2.9
Sept.	1.55	98	42	54	27	58	56	3.1	2.0

[a] Values represent means for all seepage stations.

Table A-6. Ambient air concentrations at McCloud Lake, August-September, 1982.

Date	SO_4^{2-}	NH_3	HNO_3	SO_2	NO_2
	- All values in ug/m^3 -				
8/13	3.46	0.509	0.227	N/A	N/A
8/15	1.27	0.154	0.186	N/A	N/A
8/17	2.56	0.471	0.343	1.59	6.28
8/19	1.24	0.194	0.175	1.42	7.42
8/20	2.07	0.410	0.203	1.13	5.14
8/22	1.51	0.297	0.150	2.71	5.14
8/25	3.99	0.102	1.611	2.58	10.28
8/26	1.51	0.075	0.632	2.97	1.71
8/28	6.87	1.816	0.191	3.57	4.00
8/29	1.50	0.148	0.639	1.52	4.57
8/31	3.28	0.192	1.341	4.34	4.57
9/1	3.09	0.248	0.696	1.55	10.28
9/10	2.03	0.204	0.764	4.57	13.70
9/12	3.57	0.671	0.309	7.02	5.71
9/15	1.91	0.248	0.136	2.10	2.86
9/17	2.06	0.258	0.272	2.93	6.28
9/18	2.16	0.562	0.215	3.62	9.71
9/20	4.12	0.672	1.003	8.78	3.43
9/21	3.20	0.430	0.216	0.79	1.71
9/22	2.30	0.175	0.302	1.12	7.42

BIOGRAPHICAL SKETCH

Lawrence Alan Baker was born on March 30, 1951, in Louisville, Kentucky. He was raised in New Martinsville, West Virginia, on the banks of the Ohio River. After graduating from Penn State University with a B.S. in biology in 1973, he worked briefly for the Pollution Control Division of the City of Houston, Texas, Health Department, then returned to graduate school where he first studied biology, and then environmental engineering. In 1981, he received a M.S. in environmental engineering from Utah State University and began doctoral studies at the University of Florida.

Soon after completing his Ph.D., he will marry Nancy Ann Rodenberg and will begin working as a post-doctoral fellow at the University of Minnesota.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy

J. F. Heaney, Chairman
Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy

P. L. Brezonik, Cochairman
Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy

G. R. East
Research Scientist of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy

G. Litton
Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate in scope and quality, as a dissertation for the degree of Doctor of Philosophy

D Graetz
Professor of Soil Science

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy

April 1984

Dean, College of Engineering

Dean for Graduate Studies and Research